

Traffic-Related Metals in Soil and Sediment in Mauritius

Trafikrelaterade metaller i jord och sediment
på Mauritius

Liselott Petersson

ABSTRACT

Traffic has been identified as a significant heavy metal polluter of roadside soils, and copper (Cu), lead (Pb) and zinc (Zn) in particular are associated with road travel. In a historic perspective, the Pb contribution from anthropogenic sources to nature has predominantly been a result of fuel combustion. There are indications that Cu (mainly through braking system) and Zn (emissions from tires) released from traffic give rise to as much as half of the total urban contribution of copper and zinc to the environment.

Concentrations of Cu, Pb and Zn in roadside soils and sediment have been determined at selected roads within the Grand River North West watershed in Mauritius. As total metal concentrations are not a suitable indicator of the metal concentrations that are potentially available to biota, metals extractable in 0.5 M HCl have been determined along with total concentrations. The spatial variation in metal concentration along soil transects perpendicular to roads were investigated, as was the variation with depth. Observed Pb and Zn concentrations exhibited elevated levels in topsoil in the immediate vicinity of roads with relatively large traffic densities, but the decrease in concentration with distance was rapid. Results from soil reference sites pointed to a large scale Pb pollution on the island. In comparison, observed Cu concentrations could not be assigned any influence from traffic at the selected study sites.

In the event of rain, metals contained in polluted road dust and soil may be released into soluble form, or flushed from roadways as particulate matter, and transported to nearby water courses. In Mauritius, this is of particular importance as sediment in rivers eventually may be deposited in the sensitive coastal areas of the island. However, results do not indicate that there were any elevated levels of heavy metals in sediment close to roads that were investigated in this study.

Although Cu concentrations in roadside soils did not show any enrichment and the zone of elevated Pb and Zn concentrations was not wide, there is a concern that the continuing rapid increase in the number of vehicles in Mauritius will change the situation, possibly resulting in greater impact on the surrounding environment. Hence, in order to avoid any ecological damage, it is desirable to continue monitoring the situation along highways in the country.

Key words: Copper, lead, zinc, traffic pollution, heavy metal contamination, background concentrations metals, Mauritius

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REFERAT

Trafik utgör en stor föroreningskälla av tungmetaller i vägnära jordar och särskilt är det koppar (Cu), bly (Pb) och zink (Zn) som associeras med fordonstrafik. I ett historiskt perspektiv härrör blyutsläpp främst från bränsleförbränning, medan kopparemissioner (i första hand från slitage av bromsbelägg) och zinkutsläpp (från däck) från trafik står för så mycket som hälften av det urbana utsläppet av koppar och zink till omgivningen.

Koppar-, bly- och zinkkoncentrationer i vägnära jord och sediment undersöktes inom avrinningsområdet för Grand River North West i Mauritius. Eftersom totalmetall utgör en dålig indikator på den mängd metall som finns potentiellt tillgänglig för biota användes extraktion med hjälp av 0.5 M HCl tillsammans med totalkoncentrationer. Den rumsliga variationen längsmed transekt vinkelrätt mot vägar undersöktes liksom variationen med djupet. Observerade kopparkoncentrationer var jämförbara med bakgrundsnivåer. Till skillnad från Cu var koncentrationer av Pb och Zn förhöjda i den omedelbara närheten till vägar med relativt stor trafikintensitet, men halterna minskade snabbt med avståndet. Resultat från platserna för jordreferenser visar på storskalig förorening av Pb på ön. Uppmätta kopparkoncentrationer kunde inte knytas till trafikens påverkan.

Vid regn kan metaller som finns i förorenat vägdam och förorenad jord övergå till löslig form, eller sköljas bort i partikulär form, och transporteras till närliggande vattendrag. I Mauritius är det här av speciell vikt eftersom flodsediment till slut kommer att deponeras i de känsliga kustområdena som omger ön. Dock tyder inte resultaten på förhöjda metallhalter i sediment nära de studerade vägarna.

Även om erhållna resultat av Cu inte visar på någon förhöjning och zonen med hög förorening av Pb och Zn är relativt smal, är det angeläget att följa utvecklingen eftersom antalet fordon växer snabbt i Mauritius, vilket kan förändra dagens situation och ge upphov till större miljöpåverkan. För att undvika eventuella ekologiska skador är det därför av stor vikt att i fortsättningen övervaka situationen längs landets vägar.

Nyckelord: Koppar, bly, zink, trafikförorening, tungmetallförorening, bakgrundshalter metaller, Mauritius

PREFACE

This thesis formed part of a link programme between the Department of Limnology at Uppsala University and the University of Mauritius. The coordinator for the link is Dr Anna Brunberg, Department of Limnology, Uppsala University in Sweden and in Mauritius Dr Deolall Daby at the Department of Biology, Faculty of Science, University of Mauritius has the same role. Financial support was given by the Linneaus-Palme foundation.

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1 INTRODUCTION

The rapid economic growth of Mauritius has resulted in a fast increase in the number of vehicles in the country over a short period of time. As this trend seems to continue, and utilization is constrained to a limited area, it is of interest to study the contribution of traffic-related heavy metals discharged into the environment and the potential hazard they may pose to soils and watercourses. Heavy metals commonly associated with traffic pollution are (Cu), lead (Pb) and zinc (Zn). In this context, emissions of Cu mainly originate from car braking systems, while Pb is prevalent in petrol and Zn is discharged from tires and galvanized details of vehicles. Metals occur naturally on earth, but in excessive amounts they might be harmful to plants and living organisms. As they are not degradable, they may remain in the environment for a long time, possibly causing damage also long after the source of origin have ceased.

Previously, some studies at the University of Mauritius have been conducted on mainly lead found in street dust or just next to highways. The spatial variation of traffic-related metals has not yet been investigated. When studying the environmental impact of metals on soil and sediment, it is relevant to look into what form they appear in the environment, their speciation. This reveals information on how easily metals may be mobilized, i.e. released into soil solution and available for plants and biota.

The object of this study is the Grand River North West drainage area, which is Mauritius' most industrialized basin and hosts some of the busiest roads in the country. There is currently a prevailing problem with congestion along certain highways in this part of the country, and as the number of vehicles most certainly will increase in the near future, the impact from roads can be expected to grow. Some of the watercourses in the basin of interest are used for drinking water and eventually drain into the sensitive areas of coral reefs that surround the island, where there may be risk for severe damage.

1.1 AIM

The aim of this study was to quantify the spatial variation of copper, lead and zinc, originating from vehicles in tropical soils and river sediments in the close proximity to selected roads, and to investigate their mobility in soils. This was studied in the busy catchment area of Grand River North West in Mauritius. Background information on the natural presence of metals in soils in Mauritius is rather vague, hence the ambition of this work was also to provide some reference data on background concentrations of Cu, Pb and Zn on the island.

2 MAURITIUS

Geography and geology

Situated in the Indian Ocean, east of Madagascar, the island of Mauritius stretches about 60 km in the north-southerly direction and 50 km from west to east (20 °S and 57 °E), see Figure 1. The total area is 1850 km² which is about 60 % of the area covered by Sweden's largest island, Gotland. Mauritius was created by a series of volcanic eruptions starting about 10 million years ago. Basaltic rocks dominate the island but along the coastline carbonate formations can be found. The landscape is made up of the central plateau, where much of the urban activities are located, surrounded by the lowlands which are mainly used for agricultural activities. The dominating feature of the island is sugar cane fields, which was the main export product for decades. Approximately 46 % of the country's area is allocated to agriculture, 20 % is occupied by built-up areas and 2 % by public roads. The remaining area consists of forests, grazing lands, reservoirs, swamps etc. (Central Statistics Office, 2005a).

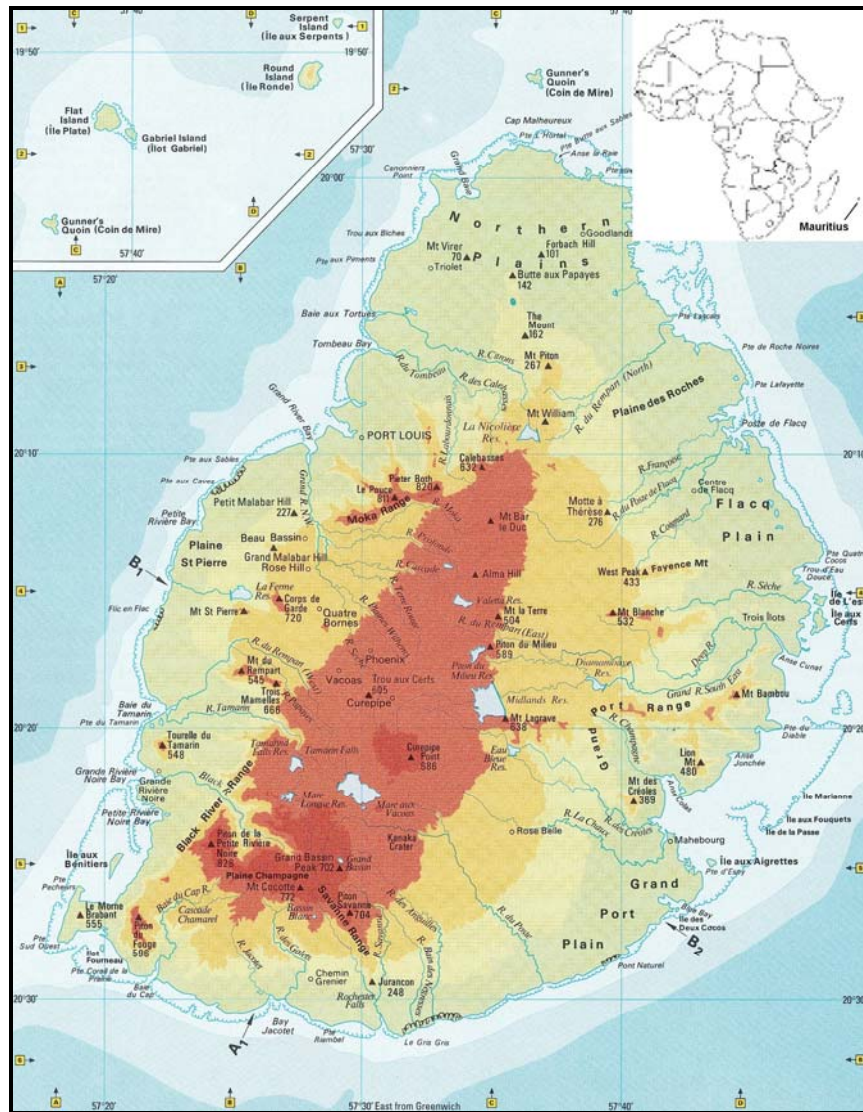


Figure 1 Map of Mauritius (modified from Atlas of Mauritius, 2002).

Population

With a population of approximately 1.2 million people, Mauritius is one of the most densely populated areas in the world, having 593 persons per square kilometre according to the United Nations (2005). During the 1980s the Mauritian economy successfully underwent major structural changes, where sugar cane made space for industrial activities such as textile manufacturing, food processing and light industry as well as tourism development. Today, the textile industry employs the greatest number of people. In 2003 more than 100 000 persons were employed for industries producing articles of clothing and about 40 000 people were working within social services and education. Approximately 23 000 people were at the same time engaged in the agricultural sector and the figures for hotels and restaurants as well as public administration were a little smaller (Central Statistics Office, 2005b).

Climate

According to Köppen's classification two main classes of climates are found on Mauritius; a humid tropical class A, for which the year's coolest month has a mean temperature above 18 °C, and a class C for which the same figure is below 18 °C. The boundary between the two classifications is at about 400 metres above sea level on the windward (east) side and 450 metres above sea level on the leeward (west) side of the island (Proag, 1995).

The mean annual temperature in Mauritius is 20-22 °C but varies greatly with altitude. Temperatures during the warmest month, February, are typically about 22 and 28 °C for the central plateau and Port Louis on the west coast, respectively. The same places reach temperatures of 17 and 22 °C, respectively, during August, which is the coldest time of year.

Two seasons are distinguishable throughout the year. Summer lasts from November to April which is the rainy period, February and March having the highest precipitation. May through October make up the winter season, which for the most part is dryer and colder than the summer. Due to the highly varying altitudes on the island, the climate changes rapidly as one travels through the country. For example, the annual rainfall in Mauritius varies from less than 800 mm in the western part of the country to above 4 000 mm in the central plateau, while the east coast annually receives approximately 1 600 mm (Water Resources Unit). The high altitude is responsible for the great amount of annual rainfall in the central parts. The rich summer rainfall arises from low pressure troughs, weak depressions and occasionally tropical cyclones that pass the island. When cyclones pass close by Mauritius, intensive rainstorms are common and rainfall of 812 mm in 24 hours has been recorded (Proag, 1995). The mean annual precipitation for Mauritius is estimated at 2 100 mm.

Like precipitation and temperature, evaporation is also a function of altitude. Mean annual potential evaporation varies from more than 1 870 mm in the northern and western coastal areas to approximately 1 370 mm in the high altitudes areas (Proag, 1995). During the summers, evaporation exceeds precipitation whereas the situation is reversed during the early winter months (Berg, 2004). Humidity is constantly high, on average about 80 % and is relatively constant throughout the year (Proag, 1995).

A dominating feature affecting the climate in Mauritius is the southeast trade winds, which prevail for a long time during the year. This direction can be detected especially

for high wind velocities. October and November are generally the calmest months while February and March normally experience a lot of wind (Proag, 1995).

Hydrology

In Mauritius there are five main aquifers that contribute to groundwater resources. In addition to wells that supply groundwater, water for irrigation, domestic use, and industrial supply is also extracted from the 11 reservoirs that exist on the island. Mare aux Vacoas and Midlands Dam, which have the capacity of storing maximum 26 Mm³ of water each, are the largest ones. Having a history of volcanic eruptions, the drainage pattern for major rivers found in Mauritius is radial. The island has been divided into 25 major drainage basins, of which the Grand River South West with an area of 166 km² is the greatest, and 21 minor drainage basins.

The traffic situation

At the end of 1993 the National Transport Authority had about 170 000 vehicles registered (IEL, 2005), which had expanded to 283 710 registered vehicles at the end of June 2004. This corresponds to a 1.7 fold increase in the last decade and from only January to June there was an increase of 2.7 %. Of the total fleet, 45 % were motorised two wheelers, 40 % cars and dual purpose vehicles and 15 % were comprised of vans, lorries, trucks, buses, etc. (Central Statistics Office, 2005c). With a population of about 1.2 million people, there were in 2004 approximately 236 motor vehicles per thousand inhabitants in Mauritius. Despite the number of vehicles increasing rapidly, this figure is much smaller than the corresponding value in Sweden. 4 220 528 cars were registered during the month of July 2005 in Sweden (Statistics Sweden, 2005), which equals 468 cars per thousand people. The difference between the two countries is even more evident when one considers that the Swedish figure does not include other vehicles than private cars, which is the case with the Mauritian figure. Considering land area, about 61 cars per km² are found in Mauritius whereas there are only 9 cars per km² in Sweden.

The commercial area of Port Louis and its surroundings draws about 60 000 workers every day (Central Statistics Office, 2005d). Having a large number of vehicles travelling towards this area during morning and evening peak hours results in heavy congestion in the Grand River North West catchment area. Not only is this a problem that causes annoyance among travellers and an increase in accidents, but it may also lead to more harmful effects on the environment than if the traffic had ran smoothly. Efforts are being made to solve the problem, but so far the problem persists.

In September 2002 Mauritius introduced unleaded petrol. Petrol previously had a maximum content of 400 mg Pb/l (Government of Mauritius, 2005), while petrol today contains 3 mg Pb/l (Pathel, personal communication, 2005).

3 PREVIOUS STUDIES ON IMPACT FROM ROADS

BSc students in chemistry at University of Mauritius have previously conducted several projects within the field of lead pollution associated with roads. Veerappapillay (2000) analysed road dust from August 1999 to January 2000. It was suggested that the lead concentration in dust decreased after a rain event, but it was concluded that the concentration generally is more or less constant with time. Nonetheless, Chuckowree (2003) found that there was a decrease in lead contamination in soil between July 2002 and January 2003. During this period unleaded petrol was introduced in the country, which was suggested to have been indicated by the obtained results. Several projects have pointed to tendencies for lead concentrations to be greater on the western side of roads, probably due to the southeasterly trade winds that prevail on the island most of the year (Naga, 1998; Ranjeet, 2000; Veerappapillay, 2000). These previous studies provide useful information, but they have only analysed total lead, not taking into account how much of the lead that is potentially available for uptake by organisms. Information on how metals vary with distance from roads or with depth in the soil profile is also scarce.

A number of studies have been carried out on heavy metal contents in sediments in Mauritius, but these have not specifically had the focus on traffic. However, in the Export Processing Zone, close to the Grand River North West estuary, contamination in the estuarine sediments was considered to have arisen from extensive use of leaded petrol and lubricating oils containing zinc additives (Ramessur, 2002).

On a world-wide scale, extensive research has been carried out on the subject of lead contamination from highways. The literature discussed in Alloway (1995) proposes that, for most roads, there is a band of 15 meters on either side where Pb concentrations exceed local background levels. Several studies also put forward exponential relationships between the content of Pb in soil and distance from roads, having large particles deposited within 5 m of the road and smaller particles transported up to 100 m.

Having a similar geology as Mauritius, comparable studies carried out on Hawaii are of great interest. Heinen De Carlo and Anthony (2002) examined soils as well as stream sediments when assessing the spatial and temporal variability of trace elements in an urban watershed on Hawaii. Compared to continental background levels, soil concentrations of Cu and Zn were elevated, though the difference was explained by the origin of the soils in the two locations. Granite and carbonate rocks naturally occur with low abundances of trace metals, while the high concentrations found on Hawaii were considered characteristic of the subtropical Hawaiian soils which are derived from weathering of basalt rocks. From a review of existing documentation of trace metal data in common rocks on Hawaii, the authors concluded that concentrations of Cu and Zn ranged between 70-167 mg/kg and 99-204 mg/kg respectively. However, regarding Pb, common Hawaiian rocks exhibited concentrations of less than ~8 mg/kg. The elevated concentrations of Cu, Pb and Zn found in the surface soil were explained by the metals' strong affinity for oxide surfaces, and there was a general decrease in concentrations with depth. Road runoff was thought to be the principal source of Cd, Cu, Pb and Zn in soils and in stream and estuarine sediment. Although the contribution of Pb has diminished substantially with time, the study expresses concern about the risk for increasing levels of Cu and Zn, which were attributed an increase in anthropogenic activity, e.g. road traffic.

Another study from Hawaii on metal contamination from roads was carried out by Sutherland and Tolosa (2001). They found that the greatest enrichments of copper, lead and zinc were detected in road dust itself followed by soil located closest to the road. At a distance of 50 m, enrichment in Pb and Zn was still apparent, but there was a considerable decay in concentration with distance compared to the road dust itself. Cu showed a narrower band of pollution than Pb and Zn, which they suggested might be the result of more rapid fall velocities as well as larger aerosol associations.

Similar to the study conducted by Sutherland and Tolosa (2001), lead showed the greatest degree of accumulation in the topsoil, among the metals analyzed, when assessing the correlation between metal concentration and traffic density in Nigeria (Fakayode and Olu-Owolabi, 2003). The level of Pb contamination decreased rapidly with distance and at a distance of 50 m from the road, the concentrations reached background levels. While concentrations of Zn and Cu demonstrated the same pattern, the levels of contamination of these metals were much smaller compared to Pb.

The contamination of lead, copper and cadmium alongside a highway in France was assessed by Viard et al. (2004) through studies of soil as well as plants and snails. The results obtained showed that pollution from the road had an impact over the entire distance studied, up to 320 m, but the peak in metal concentrations was found at a distance between 5 and 20 m from the road. The study also indicated that Pb appeared to be the most suitable metal when evaluating traffic contamination.

Not only does the vehicle density on roads determine the discharge of metals originating from traffic, but also the speed of the traffic and traffic congestion. In a comparative study of deposited dust in a large and a small urban area in the United Kingdom, great concentrations of metals were found in areas associated with junctions controlled by traffic lights (Charlesworth et al., 2003). Furthermore, a slope in the road influences metal concentrations in the surrounding environment differently depending on the direction of vehicles that travel on it. The Swedish Road Administration has recognized that emissions of especially lead and zinc exhibit greater concentrations in soils close to the lane carrying vehicles uphill as compared to soils located near the downhill slope (Vägverket, 1998).

4 METALS IN THE ENVIRONMENT

Heavy metals occur naturally in the earth's crust and may be released into the soil solution through the process of weathering. The weathering rate depends on the parent material as well as factors like climate, pH, biological activity etc. However, the factor having the greatest impact is the surface area of the particles, hence the texture is the single most important factor determining the rate of weathering (Brady and Weil, 1999).

Secondary clay minerals are created from primary mineral weathering. The most common clay minerals are kaolinites, illites and smectites. Kaolinites are the result of long and intensive weathering, comprising one silica sheet and one aluminium sheet (i.e. 1:1 mineral). Clay minerals in pure form are rarely found in soil or sediment, but are instead commonly linked to humic colloids and hydrous oxide precipitates.

In the pore water, metals may occur as free ions, and as inorganic or organic complexes. In comparison to the movement of water, metals may be transported much more slowly through the soil or sediment. The mobility of, and hence the retention time for, metals in

soils and sediments is determined by qualities of the metal itself as well as the surrounding environment. The most important chemical processes through which substances in general may be held back in the soil profile or sediment are precipitation and adsorption. However, with respect to metals, the major mechanism for determining the retention time is adsorption (Gustafsson et al., 2003). Adsorption consists of three main mechanisms: ion exchange, surface complexation, and hydrophobic adsorption. *Ion exchange* involves electrostatic attraction of free ions and results in weak bonds. A stronger form of adsorption is achieved through so-called *surface complexation*. Many cations form complexes with hydroxyl groups on surfaces of particles or with reactive groups in humus. It is especially carboxyl groups that play a major role in binding metals in humic and fulvic acids. *Hydrophobic adsorption* is also included in the adsorption processes, though this process dominates primarily when considering the adsorption of organic substances. There is generally a greater degree of adsorption on smaller grain size materials. Figure 2 shows different interactions of metals in a system.

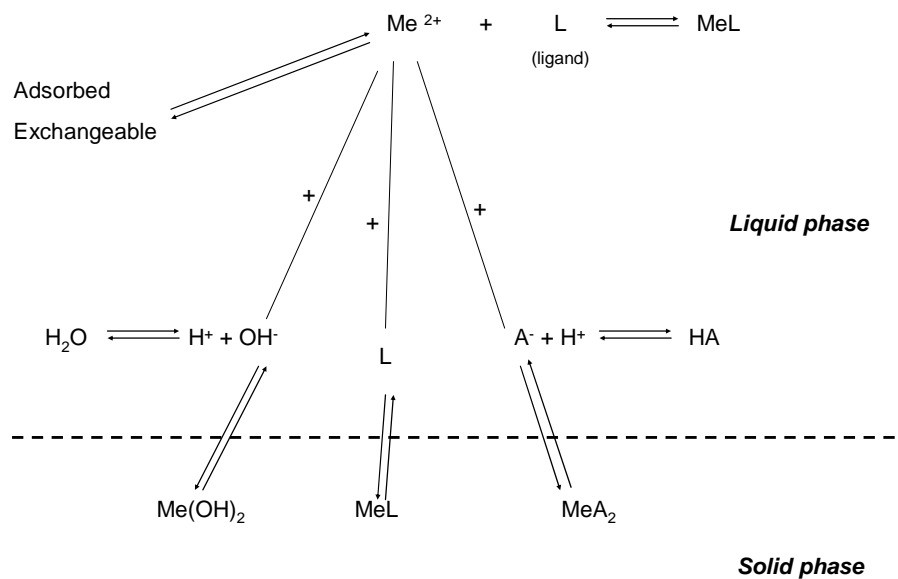


Figure 2 Chemical equilibria for a metal (modified from Alloway, 1995).

With changing geochemical conditions, metals previously immobilized by the above-mentioned mechanisms may again be released into the environment. The solubility of metal ions increases greatly with decreasing pH, which is the factor having the heaviest influence on the processes of adsorption (Gustafsson et al., 2003). The influence of pH on metal concentrations in soil depends on the fact that a great proportion of the surface charge on mineral particles are variable, changing the electrostatic attraction with changing pH.

The pH is also determining the surface complexation of organic matter. All soils contain organic matter such as living organisms, detritus, and coatings on particles, though there might be considerable differences in types and amounts of organic matter. Humus, composed of stable high molecular-weight residual products, has by tradition been

divided into (i) humin, which is insoluble in alkali and acidic solutions, (ii) humic acid, which is soluble in alkali but not in acid and (iii) fulvic acid that is soluble in both acid and alkali. These are not fundamentally different, but are distinguished from one another through different amounts of C and O in the molecules, acidity and cation exchange capacity. Metals form strong complexes with humic substances.

Oxides of iron and manganese are important factors affecting the chemical behaviour of metals in soils and sediments. They may be present as nodules, concretions, cement between particles or coatings on particles. In tropical environments, where intensive weathering has taken place, these oxides are often more abundant than clay minerals (Alloway, 1995). Metals have great affinity for oxides and this together with the fact that oxides have a large surface area results in a high degree of immobilization of metals where oxides occur.

Redox reactions are normally rather slow, but may be catalysed by the involvement of microorganisms. In anaerobic environments where sulphate reduction occurs, most metals form insoluble precipitates with sulphides. However, an increase in redox potential will result in making them unstable, mobilizing metals that might have been bound to the sulphides. The response is rather sudden and non-linear (Förstner, 2004).

A summary of metal species and associations and corresponding mobilities is seen in Table 1.

Table 1 Metal species, associations, and mobility (modified from John and Leventhal, 1995).

| Metal species and associations | Mobility |
|------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------|
| Exchangeable cations | High. Changes in major cationic composition are likely to affect adsorption-desorption processes |
| Metals associated with oxides | Medium. Increase in redox potential may cause a release, but some metals precipitate if sulphide mineral present is insoluble. |
| Metals associated with organic matter | Medium/High. Under oxidizing conditions organic matter is degraded; releasing soluble heavy metals. |
| Metals associated with sulphide minerals | Strongly dependent on environmental conditions. Oxidation of sulphides takes place under oxygen-rich conditions, leading to release of metals. |
| Metals in crystalline phase, residual | Low. Available only after weathering or decomposition. Metals from this fraction are not expected to be released within a reasonable time span. |

5 TRAFFIC-RELATED METALS

Metals commonly discussed in the context of emissions from fuel combustion as well as brake wear, tires, etc. are lead, zinc, copper and cadmium, among others. A number of studies have been carried out on the subject (Adachi and Tainosho, 2004; Davis et al., 2001; Gustafsson, 2001; Fukazaki et al., 1986; Sternbeck et al., 2002).

Having been used as an additive to fuel during decades in order to prevent uncontrolled combustion, which may reduce power and engine efficiency and might damage the engine, lead has been the subject for an extensive number of studies. Lenner and Karlsson (1998) proposed that the discharge of Pb through combustion is between 1.4 and 2.4 mg/vehicle-km, depending on type of catalytic converter used. Regarding cars without catalytic converters, it was estimated that the lead emission is 16 mg/vehicle-km.

A compilation of data made by Bækken (1993) shows that between 0.1 and 0.26 g tire wear is emitted per car and kilometre. ZnO is added as an activator during the vulcanizing process and approximately 1.8 % of the tire weight is zinc while other metals found in tires are copper, 1 % of the tire weight, and lead with 0.08 % of the weight (Bækken, 1993). Of course the proportions of components that make up tires differ with different brands. However, the degree of emission is not only dependent on the tire composition, but also on the age of tires, weather and road conditions, way of driving, etc. play significant roles. An estimation of annual emission from tires in Sweden is 150 tonnes of ZnO (Gustafsson, 2001); however, this figure is being criticized.

Brake dust consists of particulate copper as well as traces of other metals. Average concentrations of metals in braking pads have been estimated to 105 mg/g for Cu, whereas the concentrations of Pb is roughly 14 mg/g and the corresponding figure for Zn is 20 mg/g. Davis et al. (2001) indicated that the Cu discharge produced from braking systems is on the order of 75 µg/vehicle-km. It was also suggested that 89 µg Zn/vehicle-km is released and for Pb the figure is approximately 3 µg/vehicle-km. A study carried out by Garg et al. (2000) has suggested that particles released from the brake systems are rather small; about 86 % of the emission consisted of a particle size smaller than 10 µm. Estimated annual discharges of Cu, Pb and Zn from braking systems in Stockholm, Sweden, are 3 900, 560 and 900 kg, respectively (Gustafsson, 2001).

5.1 COPPER

Copper values reported for the crust of the earth range between 24 and 55 mg/kg, while total concentrations of Cu in soils are expected to be between 20-30 mg/kg (Alloway, 1995).

Copper, a metal that is not very mobile in the environment, is immobilized through strong complexes with humic acids, clay and Fe- and Al-oxides and has a tendency to form sulphides in environments where reducing conditions occur. As such stable complexes are formed, soluble humic and fulvic acids are of major importance when it comes to the transportation of copper. In addition, suspended particles play a key role when transporting copper in, for example, streams and rivers. Total Cu concentration in soil solution is about 0.01-0.6 µM, corresponding to about 0.6-38 µg/l.

Copper belongs to the group of most essential elements for plants and animals and plays a vital role for the proper functioning of many enzymes. However, overdoses can result in deposition of the metal in liver, kidney and other organs.

5.2 LEAD

According to Alloway (1995) the abundance of lead in the average crystal rock has been estimated at about 16 mg/kg, and even though natural concentrations vary to a great extent, it can be stated that Pb concentrations in uncontaminated soils in general are below 20 mg/kg.

Like Cu, Pb adsorbs very strongly to organic matter and to charged surfaces, as it has the capability of complexation with hydroxyl, carboxyl and phenol groups. Where natural or weakly amplified concentrations of lead occur, the solubility of Pb^{2+} is very low and retention time long. It has been observed that binding with predominantly organic complexes on the whole determines the transportation of lead. Gao et al. (1999) identified Pb^{2+} to form the most stable humic acid complexes of the metals investigated in this study. Like the case with Cu, the movement of lead through aquatic systems is facilitated by suspended particles. The concentration of Pb found in the soil solution is of the order of 10^{-7} M (Alloway, 1995), which is about 200 μ g/l.

Lead is present in our environment in many ways; among others the metal is a component in certain paints, it may be part of sewage sludge and pesticides and is commonly used as an additive in fuel as well as in braking systems of vehicles. To avoid uneven combustion, Pb has been added to petrol. Today, all petrol used in the country contains 3 mg Pb/l (Pathel, personal communication, 2005). No beneficial effects of lead in humans are known, but instead many adverse effects have been noticed. Even at low concentrations the metal might affect the nervous system and cause kidney dysfunction, anaemia and reproductive disorders. The target group at risk for obtaining lead in toxic concentrations is primarily children, as they might ingest soil particles.

5.3 ZINC

The content of zinc in the earth's crust is approximately estimated to be 80 mg/kg and in magmatic rocks the metal seems to be uniformly distributed, varying from 40 mg Zn/kg in acidic to a level of 100 mg Zn/kg in basaltic rocks. Estimates of background Zn concentrations in soils suggest a great range of values from 10 to 300 mg Zn/kg (Alloway, 1995).

The adsorption of Zn is a little weaker than that of lead and copper, but the value increases with increased organic and/or clay content. As a consequence of the weaker adsorption of Zn compared to Cu and Pb, this metal will often be found as the free ion, Zn^{2+} , rather than bound to organic matter in soil and surface waters (Gustafsson et al., 2003). According to calculations, the predominant species at $pH < 7.7$ is Zn^{2+} but despite the fact that Zn theoretically is more abundant than Cu or Pb in soil solution, studies have suggested that the natural concentration of Zn in the solution is as little as 4 to 270 μ g/l (Alloway, 1995).

Zinc is an essential metal as it acts as a catalytic or structural component in several enzymes taking part in energy metabolism and in RNA synthesis.

6 SAMPLING SITES

This study focuses on selected sites within the catchment area of Grand River North West, in the middle/western part of the country, which drains into the Indian Ocean at the capital Port Louis. The area covers about 115 km² (Proag, 1995) and its maximum elevation is 530 metres above sea level. The dominating feature is sugar cane fields which cover approximately 60 % of the watershed (Gustavsson, 2004). This part of the country hosts densely populated areas (according to Central Statistics Office, the number of inhabitants in the area were 175 000 in year 2000), including the cities of Quatre Bornes, Rose Hill, and Beau Bassin. There are also some congregations of industries near the outlet of the river and in the area of Phoenix in the upper part of the watershed. Industries localized within the Grand River North West drainage area are among others textile, chemical and battery industries, sugar factories as well as food and beer processors.

Three main sampling sites and five reference soil sampling sites were selected within the drainage area of Grand River North West. Figure 3 shows the locations of all sampling sites. Below follows first a brief description of soils that appear at the sites and then the main sampling sites are described. Information on soil reference sites is found in Appendix 1.

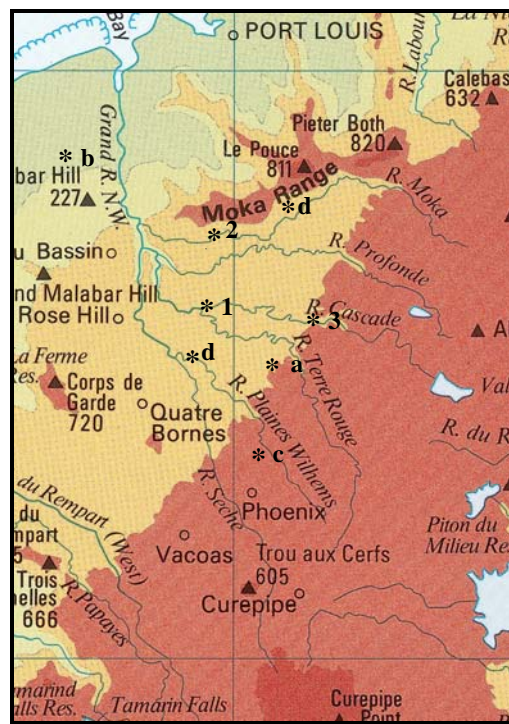


Figure 3 Map over sampling sites. Modified from Atlas of Mauritius (2002). Notations in the picture:

Main sampling sites:

- 1: Rduit
- 2: Moka
- 3: Camp Auguste

Reference soil sites:

- a: Bagatelle
- b: Chebel
- c: Henrietta
- d: Le Pouce
- e: Trianon

6.1 REDUIT

This sample site is located next to the motorway, called Bel Village-Phoenix Trunk Road, that crosses the country, connecting the airport in the south west with Port Louis and the tourist area in the north. It is situated close to Cyber Tower I, between the roundabouts at Reduit and Trianon. The eastern side of this stretch of road is mainly covered by sugar cane plantations whereas to the west one finds a number of slip roads, in between which there are well kept grass areas. During morning and evening hours, there is heavy congestion at this particular site. Based on data from the Central Statistics Office (2005d) on movement of workers in Mauritius, it was estimated that about 30 000 working people pass this road daily.

Soil samples from this site have been collected from the western side of the road, hundreds of metres from the closest slip road (highway on-ramp or off-ramp), where the vegetation is dominated by grass and low bushes. Figure 4 shows the soil sampling site where the majority of samples were collected. The soil type at this site is low humic latosol (Soil map of Mauritius, 1962). The surrounding features are flat open areas. The transects for soil sampling were placed where the road is still wide after a slip road, and here the traffic density is not as great as the part of the motorway that constitutes the main motorway. Therefore samples representing soil very close to the highway were collected further north, where the slip road had joined the main part of the highway completely. At this site, placement of the entire transects was not possible due to dense vegetation a few metres away along the road. It has to be kept in mind that this stretch of the road has a gentle slope, and the vehicles in the lane closest to this sampling point travel downhill. This implies that these samples might not reflect a representative level of contamination for this road, but rather they will reveal the “smallest concentration” of metals corresponding to this traffic density. The flat surroundings might have been exposed to the southeasterly trade winds, possibly resulting in slightly overestimated concentrations.



Figure 4 The soil sampling site of Reduit. Mr Viswah Ramsahye and Liselott Petersson.

(Photo: Ida Franklin)

The highway crosses River Cascades about 800 m south of the Redit roundabout. The river is rather big but nonetheless it is partly dry during the months when precipitation is scarce. The catchment area for this point covers approximately 20 km². Altogether eight sediment samples were collected in this river. The two samples collected upstream, approximately 200 m from the bridge, were considered unaffected by the motorway. About 15 m east of the road is a small dam with a gauging station where the Water Resources Unit (WRU) monitors the water discharge of River Cascades. This is where two other samples were collected. Figure 5 is a photo capturing the bridge of interest at this sampling site, viewed from the dam. Two other samples were collected just at the side of the bridge facing downstream. Even though not all of the particles released from vehicles passing on the motorway have reached the water by this point, samples are believed to represent the impact from the road to a certain extent through runoff. Further downstream, sediment collection was impossible as the riverbed consists of bare rocks, and following the river further on it runs underneath some other roads before it combines with several rivers, among which some have their origin in industrial areas. At a later occasion two more samples were collected in the dam and at the bridge.



Figure 5 The bridge at River Cascades, sampling site Redit.

(Photo: Liselott Petersson)

6.2 MOKA

This sampling site is situated on the eastern side of the road B 46 just south of Souillac Bridge in Moka, before the road makes a sharp turn to the left. On a daily basis roughly 8 000 people pass this road (estimated from Central Statistics Office, 2005d). The speed limit is lower than the highway at Reduit and there are no traffic lights or crossings nearby the site, hence traffic is mainly running smoothly on this stretch.

The surface of the ground is sloping slightly downwards from the road and the main vegetation is grass. Close to the road there are some scattered trees whose crowns are generally at such heights that they probably do not function as barriers to pollution from the traffic. For the samples collected at the furthest distance, the ground coverage consists of low bushes which might act as a cover and prevent some heavy metals to enter the soil from the air. According to the soil map of Mauritius (1962), this site is in the proximity of the border between low humic latosol and mountain complexes.

Four sediment samples were collected at the bridge on two occasions. Some 200 m upstream, samples representing sediment unaffected by B 46 were collected and sediments thought to represent the downstream side of the road were taken close by the waterfall approximately 150 m from the road. The drainage area of this site is approximately 20 km². Figure 6 shows the sampling site of Moka, the river is situated just next to the site for soil sampling.



Figure 6 The sampling site of Moka. The road is just on top of the slope and River Moka is just to the right of the view. (Photo: Liselott Petersson)

6.3 CAMP AUGUSTE

Among the roads investigated in this study, the B 48 road is considered having the lowest traffic density. It mainly runs through dense sugar cane fields and makes a sharp turn where it crosses the upper part of River Cascades. To the east of this turn, soil samples were collected and sediment samples were collected by the bridge and upstream, however downstream samples were not possible to collect as the bottom of the river was all rocks. About four kilometres downstream of this bridge is the study site of Redit, described above.

The soil type at Camp Auguste is latosolic red prairie soil (Soil map of Mauritius, 1962), which is younger than low humic latosol. The area where soil samples were collected seemed to be somewhat cultivated, but at the moment for sampling the area appeared to have been left untouched for a long time. There is, however, a risk that the soil at this site has been moved from its original site. The drainage area of this sampling site was estimated to 15 km². The sampling site is displayed in Figure 7 and the river is situated to the right of the picture.



Figure 7 The sampling site of Camp Auguste. River Cascades is just to the right.

(Photo: Liselott Petersson)

6.4 SOILS AT SAMPLING SITES

The dominating parent material for soils in Mauritius is basaltic lava rock. Generally the natural fertility in Mauritian soils is low and for crops to be grown economically, nutrients have to be added. To facilitate comparisons between sampling sites the aim was to find sites having the same soil type. Brief descriptions of the soils occurring in this project are presented below. The information is extracted from Proag (1995).

Low humic latosol

Low humic latosols belong to the mature soils which have no undecomposed minerals in the soil complex. In Mauritius they occur in the subhumid and lower rainfall zones (from 1 000 to 2 750 mm annually) that also have a distinct dry season. The depth is

deep (>100 cm) to moderate (>60 cm) and generally the internal drainage is good. The base saturation is fairly high (30-90 %). In comparison to other soils in the country, the organic content is low. The structure of the A-horizon is weak to moderately strong, and is made up by silty clay or clay where kaolinite is dominating. A characteristic feature of the low humic latosols is the presence of manganese dioxide.

Latosolic red prairie soil

Typically, the dark brown A horizon is rich in organic matter and usually contains high amounts of gravel and stone, whereas the lower parts of the profile are reddish brown in colour. As with the low humic latosols, the dominating clay material is also kaolinite (texture ranges from silty clays to clay loams) and again, base saturation is high. The soils are slightly acid to neutral. The depth of the soil is shallow to very shallow (less than 30 cm). At low rainfall levels the shallow depth and excessive drainage of the red prairie soils make them less fertile than the neighbouring low humic latosol. However, once rainfall is enough the fertility of the two soils are similar.

Mountain slope complexes

These soils have been mapped by taking the boundary of the intermediate and late lavas of the younger volcanic series and the older volcanic series. Drier slopes show brown to grey clays with good base saturation whereas the wetter slopes have reddish ferruginous silty clays and are low in base status due to the intense weathering. In some cases ferruginous concretions can be found in soils in drier areas. These soils occur where annual rainfall reaches 1 500 to 5 000 mm.

The soil at Redit belongs to the low humic latosols, and Camp Auguste which is situated upstream from Redit has latosolic red prairie soil. According to the definition latosolic red prairie soil is more shallow and richer in organic content than low humic latosols. However, these soils both have kaolinite as the dominating clay material and base saturation is high, so comparisons should be possible. The site of Moka is as good as on the border between low humic latosol and mountain slope complexes. It is assumed that this site is comparable to the others. Soil reference sites were all but one found in the area of low humic latosol, the odd one (Henrietta) belongs to the latosolic red prairie soil.

7 METHODS

7.1 SAMPLING

Soil and river sediment samples were collected in order to investigate the spatial distribution of metals from three roads crossing rivers that belong to the Grand River North West river system. The selection of the main sampling sites for soil sampling was based on information on soils, land use, traffic density and accessibility. A great portion of the catchment area is dominated by sugar cane plantations that are affected by ploughing and irrigation. Land use preferred for soil sampling was land that was neither used for agriculture nor buildings nor covered with concrete.

At each selected soil sampling site, two transects perpendicular to each respective road were identified. Along these transects, sampling was carried out at specific distances (approximately 1.5, 3.3, 5, 10, and 20 m) from each road (sometimes named *sampling points* in the following work) to see the horizontal distribution of the metals investigated. Soils from two different depths (0-5 cm and 15-20 cm) were collected in order to investigate the downward distribution of the metals. An acid pre-washed (10 % HNO₃) plastic scoop was used for sampling, and during the transport to the laboratory the collected soil samples were kept in pre-washed plastic bottles.

To provide data on background metal concentrations in soils, reference samples were collected from five sites that were considered to be affected by traffic on the island as little as possible. As it was desirable that qualities regarding soil type, precipitation, humidity etc. were as similar as the main sampling sites as possible, these sites were selected in the catchment area of Grand River North West. Again, the accessibility to each site influenced the decision on locations. Furthermore, soil samples from a depth of 50 cm were collected at three of these sites to add some information on background levels deeper down the soil profiles.

In surface waters the concentration of metals can fluctuate extensively depending on what conditions prevail in the aquatic system. Hence as concentrations in sediments do not vary to the same extent as water concentrations, sediments are often studied when assessing the quality of aquatic systems. Investigation of metal contents in sediments is therefore of interest. To examine the amount of traffic-related metals in river sediment, the intention was to collect surface sediment samples upstream, at, and downstream the locations where the selected roads cross the rivers. Upstream samples would represent sediments unaffected by traffic, at the bridges the sediment would partly consist of debris originating from surface runoff from the roads, and the downstream sediment would consist of particles from traffic that were deposited straight on the river. Again, an acid pre-washed plastic scoop was used. The upstream sediment samples were expected to be unaffected by the traffic from the road, whereas the samples from the bridges and downstream the bridges were anticipated to show the impact from the vehicles.

In total, 90 soil and 22 sediment samples were collected. All soil and sediment samples, except two sediment bridge samples at each of the main sites, were fetched on the 18th and 21st of February for Moka and Reduit, respectively, and on the 17th of March for Camp Auguste. An additional sampling of sediment was conducted at the bridges on the 11th of April as to see if there was any visible change after peak discharges in the rivers.

On the same occasion, bulk samples for the grain size analyses were also collected at the main sampling sites. Reference soil samples were collected on March 14th and April 4th. Two samples were collected at each distance and depth at the main sampling sites, at each depth at reference sites and each point for sediment sampling. From here on, these two samples representing the same location are called *doubles*.

7.2 SAMPLE PREPARATION

After sampling, soil and sediment samples were as soon as possible dried in a drying cabinet (35-40 °C) for 48 hours. They were then crushed gently with a wooden pestle in order to split aggregates but let the minerals themselves stay intact. The processed samples were then sieved through a 425 µm sieve and stored in polyethylene bags until analyses. This fraction was used for the metal analyses. Some of the samples collected were also sieved for the fraction <2 mm, which was used for analyses of organic content and pH. For the grain size analyses, one composite sample was collected at each of the three main sampling sites, consisting of the top 30 cm of soil.

7.3 ANALYSES

Today it is widely accepted that it is not possible to properly evaluate the environmental risk originating from heavy metals by only quantifying total metal concentrations. The reason for this is that total concentrations of metals are poor indicators of bioavailability and environmental impact (Chandra Sekhar et al., 2004; Ramirez et al., 2005). By using different reagents a picture can be obtained of how strongly metals are bound in sediments and soils. In order to receive an adequate metal characterization, Gismera et al. (2004) suggest the combination of at least two reagents. Tessier et al. (1979) established a technique for the partitioning of metals in sediment and soil, dividing particulate trace metals into (i) exchangeable metals, (ii) metals bound to carbonate, (iii) metals bound to iron and manganese oxides, (iv) metals bound to organic matter and (v) metals in the residual form. The different extractions simulate various environmental conditions to which soil and sediment may be subjected. This method, or modifications from it, has been broadly used in environmental contexts. In this project, the speciation of copper, lead and zinc in soil samples was determined for three fractions: exchangeable and easily soluble metals, bioavailable metals, and total metals. Sediment samples were analyzed for bioavailable and total metal fractions. The selected techniques are described below.

Exchangeable and easily soluble Cu, Pb and Zn

For extraction of exchangeable and easily soluble Cu, Pb and Zn, ammonium acetate, NH₄OAc, has been extensively used. However, Tessier et al. (1979) among others have confirmed that this reagent might also attack metals attached to carbonates. Instead, magnesium chloride, MgCl₂, was selected for analysis of this fraction. Soil samples were extracted using 1 g of each sample with 10 ml of 1 M MgCl₂ and shaken on an orbital shaking table, IKA HS 260 basic, at 210 rpm at ambient temperature for one hour (Tessier et al., 1979). Following the extraction the solutions were filtered, using Whatman No 1 filters, into volumetric flasks. Each sample was then diluted with distilled deionised water to 25 ml. The diluted samples were transferred into 50 ml bottles and subsequently analysed with flame atomic absorption spectrometer (F-AAS, Unicam 929).

Bioavailable Cu, Pb and Zn

All collected samples were analysed for bioavailable metals. Sutherland et al. (2004) recommend 0.5 M HCl as an optimal treatment procedure for assessing bioavailable metals in solid media and the method has been used by several workers (Kominar, 2005; Gillian, 2005) when assessing bioavailable heavy metals in sediment. This extraction removes adsorbed metals but does not remove Cu, Pb and Zn from the matrix of the primary minerals. 1 g of soil was mixed with 10 ml of 0.5 M HCl, and then shaken on an orbital shaking table for 18 hours. Following the extraction the solutions were filtered, using Whatman No 1 filters, into volumetric flasks. The solutions were filled to 25 ml with distilled deionised water. Analyses were done with F-AAS. The pH was controlled to be below 2 prior to and after extraction.

Total Cu, Pb and Zn

At the main sampling sites, analysis of total Cu, Pb and Zn was performed for samples collected closest to respective road and at the furthest distances. The purpose of this was to make comparisons to earlier results from Mauritius and to estimate the amount of total metals that were found in the bioavailable form. Analysis of total metals for reference sites was conducted for three soil samples collected from a depth of 50 cm. For the analysis a method was used that had been used in previous studies carried out by students at University of Mauritius. 0.5 g of soil was digested in acid pre-washed teflon vessels using 2 ml HF and 5 ml HNO₃ in a High Performance Microwave Digestion Unit (Milestone, mls 1200 mega, microwave digestion rotor MDR-600/10 type). The program for digestion was 250 W and 400 W for 5 minutes each, followed by 500 W during 10 minutes, and finally the microwave was ventilating for 10 minutes. The rotor with the samples was then placed in a cooling bath for about 30 minutes. Subsequently the contents of the vessels were filtered into volumetric flasks, diluted to 25 ml with distilled deionised water and analysed with F-AAS. Soil samples from the sites at the closest and furthest distance from the roads were analysed for total metals.

Plastic and glassware utilized in the metal analyses were acid washed in 10 % HNO₃ prior to use and care was taken not to contaminate samples by using metal equipment. Samples were analyzed using an F-AAS at the Department of Chemistry, University of Mauritius. For digestion and extraction procedures, reagent blanks were prepared in order to disclose any possible contamination in the reagents being used. Quality control was achieved by analyzing a blank for every ten samples, and then verifying the result against the standard curves of each metal. Also all samples, doubles, collected in the field were divided into *duplicates* in the lab and analyzed separately. This meant that for one specific point four results were obtained in the metal analyses.

Particle size distribution

Particle size distribution was determined through the wet sieving method according to British Standard (BS 1377: Part 2: 1990). Soil from the top 30 cm was collected from each of the main sampling sites (three samples) and the samples were oven-dried overnight at a temperature of 110 °C. Approximately 500 to 600 g of each soil sample was then mixed with about 500 ml sodium hexametaphosphate (2 mg/l) and left for 24 hours in order to disaggregate the soil. Thereafter, the soaked samples were washed on a 63 µm sieve and the soil retained on the sieve was put in the oven to dry (110 °C). The following day, the mass of each soil was noted and dry sieve analysis was carried out using sieves down to 63 µm. The mass on each sieve was recorded. This size represents the division between fine sand and smaller particles as silt and clay according to Canada

Soil Survey Committee. Unfortunately, due to time constraints, analysis of finer grain sizes, which are important when discussing metal content in soil, could not be performed. Making the assumption that the soils have got similar distribution in grain sizes $<63 \mu\text{m}$, the measured silt and clay levels may still be used for comparisons between the soils.

Loss of ignition and pH

To get a clearer picture of the situation in the three main sampling soils, and to facilitate the interpretation of the metal analysis, some further analyses were carried out. Particle size analyses as well as loss on ignition were carried out in the Metallurgy Laboratory in the Mechanical Engineering Department, while pH measurements were done at the Chemistry Department.

To get an idea about the organic content in the soils, upper and lower samples from distances of 3.3 and 10 m from each road were analysed for loss on ignition (LOI). LOI was also investigated for reference samples. Crucibles were first oven dried at $110 \text{ }^\circ\text{C}$ and their weights were noted. Then roughly 5 grams of soil was added to each crucible. Thereafter the samples were put into an unheated muffle furnace, which was then heated to $440 \text{ }^\circ\text{C}$. After 4 hours in the furnace, crucibles were taken out to cool in a desiccator. When the samples had cooled down they were weighed again and the organic content for each sample was calculated.

The samples used for LOI were also examined for pH. Commonly, water, potassium chloride or calcium chloride is used for the determination of soil pH. Calcium chloride, CaCl_2 , has several advantages to the other solutions (Carter, 1993):

- it gives a fairly good approximation for field pH for agricultural soils
- up to one year of storage of air dry soil does not affect pH
- pH is not affected by the soil-to-solution ratio used

As not all soil samples had been stored for the same amount of time, the decision was made to use calcium chloride for this project. 25 ml 0.01 M CaCl_2 was mixed with 5 g of soil. Samples were shaken vigorously for 10 minutes on an orbital shaking table. The soils were then allowed to settle for approximately 14 hours before pH was measured.

All analyses were performed at the University of Mauritius during March, April and May 2005.

Hydrological data

The discharges in the rivers at the main sampling sites were greater than average discharges during the period of sampling and might have had an effect on the amount of sediments in the rivers. To get an idea about the situation, discharge data was collected from the WRU. Data on rainfall during the period of sampling was obtained from the Mauritius Meteorological Services. Rainfall data was found at stations in the vicinity of each of the three main sampling sites; Reduit, Moka and Cote d'Or (Camp Auguste).

7.4 TOOLS FOR INTERPRETATION OF RESULTS

In the literature there are some methods to examine the impact from human activity on soil or sediment described, but there is no widely accepted standard being used. One way of assessing the anthropogenic impact is to use reference samples from an area that is considered unaffected from anthropogenic pollution. Standardising the metal levels in soils from the main sampling sites with reference levels was done for both bioavailable and total concentrations, as shown in Equation 1.

$$Ratio = \frac{[M]}{[M]_{ref}} \quad (\text{Equation 1})$$

Systems for classification of polluted soils and sediments have been developed by the Swedish Environmental Protection Agency, EPA. Guideline values for soil consider the most sensitive land use and if concentrations exceed them, there is a risk to human health and/or environment. The reference values for contaminated sites used, on the other hand, represent the concentrations of metals that would have existed if there was no impact of a local point source (i.e. diffuse pollution spread over a large scale is included here). Table 2 shows guideline and reference values set by the Swedish EPA (Naturvårdsverket, 2005a) together with some concentrations presented in the previous sections.

Table 2 Comparable values on metal concentrations in soil [mg/kg].

| | Guideline values ¹ | Reference values ^{2*} | World conc. Alloway (1995) | Hawaiian soil ³ ** | Hawaiian rocks ⁴ |
|-----------|-------------------------------|--------------------------------|----------------------------|-------------------------------|-----------------------------|
| Cu | 100 | 30 (25) | 20-30 | 115 (22) | 70-167 |
| Pb | 80 | 25 (25) | <20 | 13 (10) | 8 |
| Zn | 350 | 100 (70) | 10-300 | 141 (29) | 99-204 |

* Values without parentheses represent sedimentary soils, within parentheses are values for moraines.

** Figures with no parentheses are total metal concentration, inside parentheses are HCl extractable metals.

¹ Naturvårdsverket, 2005a

² Naturvårdsverket, 2005a

³ Sutherland and Tolosa, 2001

⁴ Heinen De Carlo and Anthony, 2002

Considering the low number of samples (four) representing one specific point in this study, any statistical analysis will be weak. However, using Student's t-test, attempts were made to see if there was any significant difference between (i) levels of metals in the soil closest to the roads and the soil collected furthest away at each site, (ii) concentrations found in the upper layers and samples from lower soil layers, (iii) samples from the main sampling sites, both total and bioavailable concentrations and (iv) the levels of metal found at main sites and reference sites.

Results from earlier studies on the contribution of metals from traffic were compiled and used for comparison. The University of Mauritius has previously done some research on Pb along roads, for example along the stretch of the motorway between Reduit to Port Louis.

Estimations of the levels of copper, lead and zinc that can be expected from vehicles at Redit and Moka were made using data on the amount released particles per car and km and movement of people across the country. These values were then compared to the measured concentrations.

Reference values for contaminated surface sediments (0-1 cm) found in Table 3 are based on the distribution of concentrations found in Swedish lake sediments (Naturvårdsverket, 2005b). Class 1 through 3 include 95 % of the basic data collected in Sweden. Samples that fall in class 4 or 5 are mostly found in locally polluted areas. Class 5 has only been recorded in isolated locations in the country.

Table 3 Reference values for lake sediment (Naturvårdsverket, 2005b).

| Class | Risk for biological effects | Cu [mg/kg] | Pb [mg/kg] | Zn [mg/kg] |
|--------------|------------------------------------|-----------------------|-----------------------|-----------------------|
| 1 | No or low risk | < 15 | < 50 | < 150 |
| 2 | Small risk | 15-25 | 50-150 | 150-300 |
| 3 | Risk evident | 25-100 | 150-400 | 300-1000 |
| 4 | Increased risk | 100-500 | 400-2000 | 1000-5000 |
| 5 | Risk at short exposure times | > 500 | > 2000 | > 5000 |

When comparing metal concentrations in this study with the Swedish EPA reference and guideline values, it should be kept in mind that the Swedish EPA values are based on digestion with 7 M HNO₃. This digestion includes metals bound in insoluble Al-, Fe- and Mn-oxides and sulphides as well as organic matter with complex matrices that are left out when using 0.5 M HCl. Hence, metal concentrations in this study can be expected to be smaller than if 7 M HNO₃ would have been used.

8 RESULTS

8.1 CHEMICAL ANALYSES

For each sampling point, two samples were collected in the field. As these were divided into duplicates in the lab, four results were obtained from each sampling point in the chemical analyses. The averages of copper, lead and zinc for the sampling points are presented below. For the complete list of results from individual samples (doubles and duplicates), turn to Appendix 2.

Exchangeable and easily soluble metals

Extraction for exchangeable and easily soluble metals as well as bioavailable metals was feasible for 40 samples on each occasion. All samples in the first set that were analysed for exchangeable and easily soluble metals showed concentrations of metals below detection limits. Among these samples were those that had been collected closest to the highway at Reduit and therefore were expected, if at all, to show the greatest concentrations of this fraction among the samples. Detection limits with F-AAS for copper, lead and zinc are 1.5, 15, and 15 µg/l, respectively (Plumlee et al., 1999, pp 268-269), which translates to solid phase concentrations of 0.075, 0.75, and 0.75 mg/kg, respectively. As these figures are extremely low, no further analysis of exchangeable and easily soluble metals was conducted.

Bioavailable metals

Results from the analysis of average bioavailable metals in soils from the reference sites are shown in Table 4. Soil samples from a depth of 50 cm were collected only at three of the sites. Average copper concentrations detected at the reference sites were between 17 to 41 mg/kg and did not show any remarkable variations between sites or depths. However, in the individual samples, the Cu range was between 7 and 72 mg/kg. The range for lead was from below detection limits to 58 mg/kg, with the average being 7 to 36 mg/kg. Zn showed the greatest variation of the reference samples; levels were found to be between the detection limit and 204 (!) mg/kg. It is notable that the site of Bagatelle distinguishes itself remarkably as compared to the other sites regarding the average levels of Zn.

Table 4 Average bioavailable metal concentrations at reference soil sites. “Upper” denotes samples from depth 0-5 cm, “Lower” 15-20 cm and “Deep” samples at 50 cm depth.

| | Cu [mg/kg] | | | Pb [mg/kg] | | | Zn [mg/kg] | | |
|------------------|------------|-------|------|------------|-------|------|------------|-------|------|
| | Upper | Lower | Deep | Upper | Lower | Deep | Upper | Lower | Deep |
| Bagatelle | 26 | 26 | - | 28 | 16 | - | 97 | 154 | - |
| Chebel | 26 | 26 | - | 12 | 7 | - | 27 | 20 | - |
| Henrietta | 17 | 17 | 41 | 26 | 41 | 9 | 5 | n d | 14 |
| Le Pouce | 36 | 29 | 20 | 16 | 33 | 9 | 8 | 6 | n d |
| Trianon | 32 | 31 | 34 | 16 | 33 | 12 | 15 | 10 | 16 |
| Average | 28 | 26 | 31 | 20 | 26 | 10 | 31 | 47 | 15 |
| Average* | 28 | 26 | 31 | 18 | 29 | 10 | 14 | 12 | 15 |
| Std.dev. | 8.5 | 13 | 10 | 13 | 40 | 2.3 | 37 | 61 | 3.7 |
| Std.dev.* | 8.0 | 5.9 | 10 | 11 | 18 | 2.3 | 9.1 | 5.8 | 3.7 |

* Bagatelle results are not included due to probable impact from earlier settlements.

n d = not detected

At Redit one can distinguish high levels of bioavailable lead and zinc in the upper soil layer in very close proximity of the road, which is illustrated in Figure 8. The decline with distance was rapid and Pb concentrations decreases faster than Zn. Analysis of copper that was available for biota in the upper and lower layers of the soil showed very similar results and no horizontal variation was distinguishable with distance from the road. Pb exhibited the greatest variation in metal concentrations; the sample with the least Pb content showed 6 mg/kg and the greatest concentration recorded exceeded 250 mg/kg. The range for bioavailable Cu was 9-48 mg/kg and Zn 12-195 mg/kg.

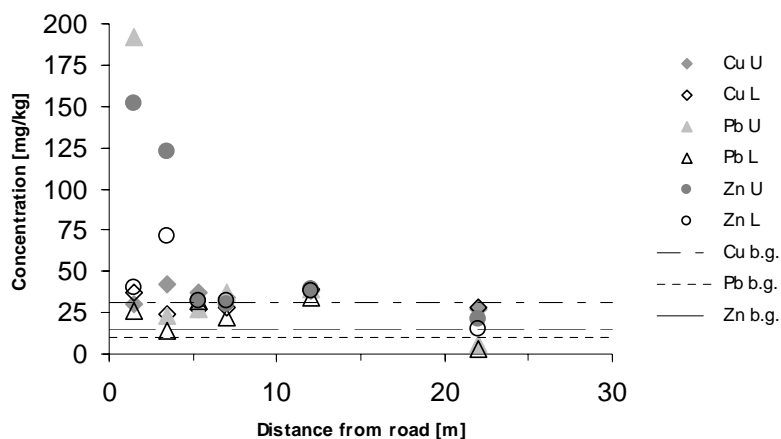


Figure 8 Spatial distribution of the averages of bioavailable metals in soil at Redit sampling site. U denotes top soil (0-5 cm), while L is from 15-10 cm depth. The lines show background concentrations.

As for the case with Redit, concentrations of lead and zinc at Moka were enhanced close the road as compared to the ones at further distances, see Figure 9. However, here the lower soil samples showed also comparatively high levels of metals. Again Pb concentrations decreased more rapidly with distance than Zn. The greatest Pb concentration recorded at Moka was 105 mg/kg, whereas levels below detection limits were recorded for the lower soil sample at the furthest distance (20 m). The range for Zn stretched from 7 mg/kg to 114 mg/kg and the corresponding figures for Cu were 25 and 62 mg/kg.

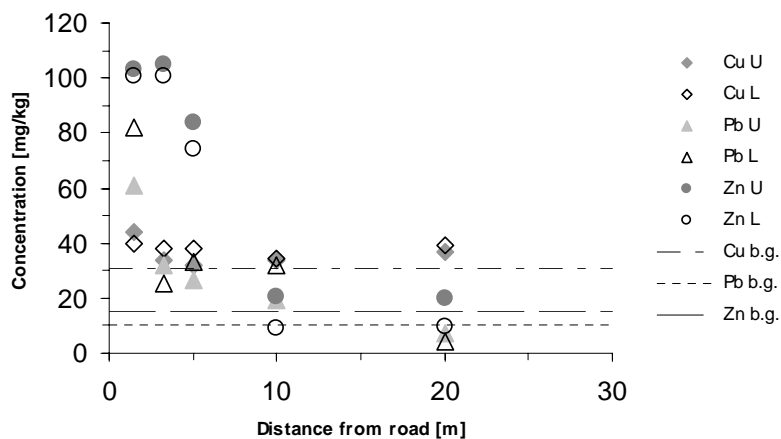


Figure 9 Average concentrations of bioavailable Cu, Pb and Zn in soil at site Moka. Samples from upper 0-5 cm are called U, samples from 15-20 cm depth are named L. Background levels are shown with lines.

Camp Auguste displayed a different pattern compared to the sampling sites at Redit and Moka, see Figure 10. For lead and zinc, levels were notably lower in the very proximity of the road as compared to the above mentioned sites. The range of Pb was 13-55 mg/kg, while Zn and Cu showed ranges of 7-29 mg/kg and 22-32 mg/kg respectively.

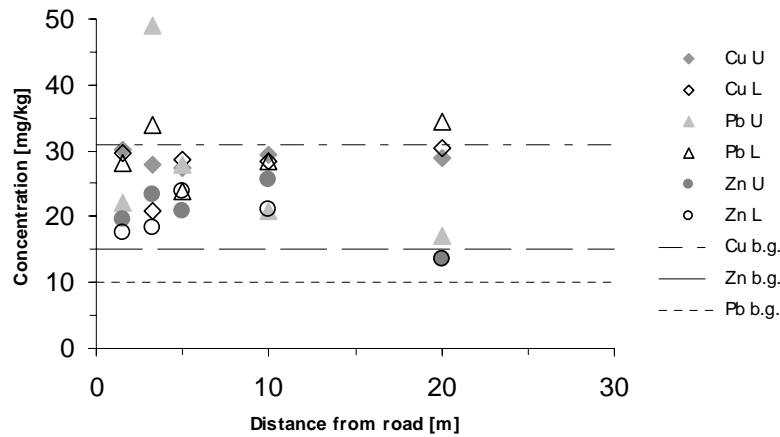


Figure 10 Distribution of bioavailable Cu, Pb and Zn (averages) in soil at Camp Auguste. U denotes samples from upper soil layer, L lower layer. Lines denote background levels.

The average results from analysis of bioavailable metals in sediments can be viewed in Table 5. Copper concentrations for individual samples exhibited a narrow range stretching from a minimum of 18 mg/kg to a maximum of 40 mg/kg. The smallest concentration, 9 mg/kg, was found at the bridge at Camp Auguste whereas a sample from the bridge at Moka contained 72 mg/kg. Levels of zinc were greatest by the bridge at Moka, reaching 118 mg/kg, and the downstream samples of Moka exhibited the smallest concentration of Zn in sediment, 17 mg/kg.

Table 5 Average bioavailable metals in sediments. Numbers denote 1st or 2nd sampling occasion.

| | | Cu [mg/kg] | Pb [mg/kg] | Zn [mg/kg] |
|---------------------|------------|-----------------------------|-----------------------------|-----------------------------|
| Redit | Upstream | 28 | 16 | 34 |
| | Dam 1 | 25 | 16 | 32 |
| | Dam 2 | 33 | 15 | 38 |
| | Bridge 1 | 28 | 25 | 31 |
| | Bridge 2 | 34 | 16 | 36 |
| Moka | Upstream | 27 | 30 | 36 |
| | Bridge 1 | 39 | 50 | 66 |
| | Bridge 2 | 30 | 24 | 104 |
| | Downstream | 29 | 15 | 36 |
| Camp Auguste | Bridge 1 | 30 | 15 | 26 |
| | Bridge 2 | 27 | 11 | 23 |

Total metals

The average total copper concentration for the deeper reference samples was 88 mg/kg and also the content of zinc was rather large at 67 mg/kg, see Table 6. Lead concentrations however, were considerably smaller, the average being 7 mg/kg. Regarding main sampling sites, average copper levels were within a range of 77 – 105 mg/kg. Lead demonstrated great deviations between concentrations in samples found in the upper layer (220 mg/kg in average) as compared to the ones found further down in the soil (24 mg/kg) at the sampling point closest to the highway at Reduit. The smallest average total Pb concentration recorded at the main sampling sites was at 20 m distance from the road at Moka (7 mg/kg) and was comparable to concentrations obtained at the furthest distance from the highway at Reduit. At Reduit as well as Camp Auguste, generally, greater total zinc concentrations were recorded in the top soil layer than in the lower layer. The maximum concentration (240 mg/kg) was again found at the 1.5 m distance from the highway at Reduit. At the Reduit and Moka sites there was a general decrease in total Zn levels with distance from respective road. The lower sample at the 20 m distance at Camp Auguste showed the smallest concentration of Zn, 71 mg/kg. In Appendix 2, the estimates of metals in the residual form (i.e. insoluble Fe- and Mn-oxides, sulphides, and silicate minerals) at different sites can be viewed.

Table 6 Average total Cu, Pb and Zn concentrations in soil at selected distances at main sampling sites. U denotes samples from 0-5 cm depth whereas L are samples from a depth of 15-20cm. Reference samples were collected from 50 cm depth.

| | Distance from road [m] | Cu [mg/kg] | | Pb [mg/kg] | | Zn [mg/kg] | |
|-------------------|------------------------|------------|-----|------------|-----|------------|-----|
| | | U | L | U | L | U | L |
| Reduit | 1.5 m | 96 | 100 | 220 | 24 | 240 | 107 |
| | 22 m | 101 | 105 | 12 | 8 | 127 | 125 |
| Moka | 1.5 m | 79 | 77 | 103 | 109 | 186 | 185 |
| | 20 m | 100 | 101 | 7 | 8 | 64 | 71 |
| C Aug | 1.5 m | 82 | 83 | 19 | 20 | 100 | 89 |
| | 20 m | 84 | 85 | 16 | 20 | 75 | 73 |
| References | | | | | | | |
| Henrietta | | | 96 | | 6 | | 74 |
| Le Pouce | | | 73 | | 6 | | 52 |
| Trianon | | | 94 | | 9 | | 74 |
| Average | | | 88 | | 7 | | 67 |

Particle size distribution

The sieving process revealed that the soils at the main sampling sites all consist of rather finely grained particles. The amount of particles smaller than 63 µm (silt and clay) for Reduit, Moka and Camp Auguste was 42, 79 and 61 % respectively.

Loss on ignition and pH

The analyses for soil pH and organic content did not show any distinguishable trend between upper and lower layers, which can be seen in Table 7. It was assumed that the organic content did not differ along transects at the main sampling sites and pH appeared to show rather random results with distance from highroads.

Table 7 pH at the soil sampling sites. U denotes upper soil layer, L soil at a depth of 15-20 cm.

| | pH | | | | Organic content [%] | |
|-------------------|----------|----------|--------|--------|---------------------|----|
| | U 3 m | L 3m | U 10 m | L 10 m | U | L |
| Reduit | 5.9 | 5.2 | 5.4 | 7.1 | 16 | 15 |
| Moka | 7.0 | 7.0 | 6.5 | 3.7 | 15 | 15 |
| C Aug | 3.2 | 6.2 | 5.1 | 6.0 | 20 | 20 |
| References | U | L | | | | |
| Bagatelle | 6.5 | 5.1 | | | 17 | 17 |
| Chebel | 6.6 | 6.6 | | | 22 | 21 |
| Henrietta | 4.4 | 3.5 | | | 35 | 33 |
| Le Pouce | 4.5 | 2.7 | | | 17 | 16 |
| Trianon | 5.1 | 6.2 | | | 17 | 16 |

8.2 ESTIMATION OF METALS RELEASED FROM TRAFFIC

A very rough estimation of the expected metal contribution from the traffic may be done with the data gathered. However, many assumptions are needed to facilitate this. Based on data from the Central Statistics Office (2005d), it has been estimated that at least 27 400 workers pass the stretch where the Reduit sampling site is located one way every workday. Of course, workers also move by bus, but to simplify the calculation only cars are included in this example. It was assumed that on average four people sit in every car and this would compensate for trips not included in this figure (private trips and students moving between cities, bus traffic, and weekend travel). This generalisation does not take into account journeys done by tourists, even though this stretch constitutes the main route through the country. With these conditions, the number of vehicles passing this stretch every day becomes 13 700. It has been suggested that the release of particles from tires is 0.1-0.36 g per car and kilometre (Bækken, 1993). Suppose the emission is 0.23 g and that the emitted particles are proportional to the metal content in tires. Since Bækken (1993) estimated the Zn content to about 1.8 %, this results in a release of about 4.14 mg Zn per car and kilometre. Bjelkås and Lindholm (1994) suggest that the emission of Zn is 3.0 mg/km, so assuming the true value is the average between these two, 3.57 mg Zn per car and kilometre is released. Considering the emission of tire-related Zn released over a 20 m stretch of road, the release will be:

$$\frac{27400 \text{ people/trip}}{4 \text{ people/car}} \cdot 2 \frac{\text{trips}}{\text{day}} \cdot 3.57 \frac{\text{g Zn}}{\text{car} \cdot \text{km}} \cdot \frac{1}{50} \text{km} = 978 \frac{\text{mg Zn}}{\text{day}} \approx 357 \frac{\text{g Zn}}{\text{year}}$$

At Moka, which has about 8 690 people and 4 343 cars with the above mentioned assumptions passing the sampling site daily, 310 mg of Zn would be released on the 20 m stretch each day (113 g Zn/year). No good estimates of vehicles was found for Camp Auguste, hence similar calculations were not made for this sampling site.

Assuming that about 1 % of tires constitutes of copper (Bækken, 1993), 630 mg Cu per day (230 g Cu/year) will be released at Reduit over 20 m, while corresponding figures for Moka are 200 mg Cu/day and 73 g Cu/year. For lead the contribution from tires are less; 50 mg Pb/day (18 g Pb/year) at Reduit and 16 mg Pb/day (6 g Pb/year) at Moka over the same stretch.

When assessing the release of metals from car brake systems the figures from Davis et al. (2001) were used. Using the assumptions mentioned previously, the release of Cu, Pb and Zn on the 20 m stretch at Redit was estimated at 20 mg, 1 mg and 25 mg respectively each day (i.e. 7 g Cu, 0.3 g Pb and 9 g Zn annually). As regards Moka corresponding daily figures were 7 mg, 0.3 mg and 8 mg, and annually the contribution would be 2 g, 0.1 g and 3 g of Cu, Pb and Zn, respectively. Assuming that cars have got catalytic converters emitting 1.9 mg Pb/vehicle-km (based on data from Lenner and Karlsson, 1998) Pb pollution originating from combustion was estimated to 500 mg per day for the 20 m stretch at Redit and 200 mg at Moka, corresponding to annual discharges of 190 g and 60 g Pb at the two sites.

Studying zinc over 20 meters perpendicular to the road, assuming that the particles distribute themselves evenly over the 20*20 m² area, the annual contribution from tires and braking systems to the top soil layer (0-5 cm) is:

$$\frac{M_{Zn, total}}{V_{soil}} = \frac{356\,970\,mg + 9\,033\,mg}{(20 \cdot 10^2)^2 \cdot 5\,cm^3} = 0.0183 \frac{mg}{cm^3}$$

Bulk density for a tropical clay and a sandy loam found in Zimbabwe has been estimated to 1.20 g/cm³ and 1.54 g/cm³ (Brady and Weil, 1999, pp 141). Presuming a bulk density of 1.37 g/cm³ is applicable on the soils found at the sampling sites of Redit and Moka this would mean that on an annual basis the expected contribution of Zn is:

$$0.0183 \frac{mg\ Zn}{cm^3} \cdot \frac{1}{1.37\ g\ soil} \cdot 1000 \frac{g}{kg} = 13.4 \frac{mg\ Zn}{kg\ soil}$$

Calculated metal contributions on a 20 m stretch along the highways at Redit and Moka during a year are compiled in Table 8. The estimated contribution of each metal in mg/kg is also presented.

Table 8 Compilation of calculated annual metal contribution to Redit and Moka over a 20 m stretch.

| | Redit [g] | | | Moka [g] | | |
|---------------------|-----------|-----|------|----------|-----|-----|
| | Cu | Pb | Zn | Cu | Pb | Zn |
| Tires | 230 | 18 | 357 | 73 | 6 | 113 |
| Braking pads | 7 | 0.3 | 9 | 2 | 0.1 | 3 |
| Fuel | | 190 | | | 60 | |
| Total | 237 | 208 | 366 | 75 | 66 | 116 |
| Contribution | | | | | | |
| mg/kg | 8.7 | 7.6 | 13.4 | 2.7 | 2.4 | 4.2 |

8.3 DISCHARGE AND PRECIPITATION DATA

The discharges obtained and calculated for the rivers at each respective sampling site are displayed in Appendix 3, together with the discharges for the same period of time for the years 1996-1999. Appendix 4 presents the daily precipitation at each site during the period of sampling. Monthly precipitation data from the sampling sites during the period of sampling and the 30 year monthly average precipitation (Padya, 1984) are displayed in Table 9. Compared to the average, heavy rains fell during March whereas April was dry at all sites.

Table 9 Monthly precipitation February-April 2005, and monthly averages in Mauritius.

| | Reduit | Moka | Cote d'Or | Average 1951-1980 |
|------------|---------------|-------------|------------------|------------------------------|
| Feb | 269 | 280 | 422 | 280 |
| Mar | 654 | 562 | 665 | 309 |
| Apr | 70 | 27 | 16 | 216 |

More than 100 mm rain fell the last three days before sampling at Moka. For the case of Reduit the same amount precipitation had fallen, but prior to the occasion of sampling there had been three rather dry days. A lot of rain also fell at Camp Auguste in February and the beginning of March but when sampling at this site took place, a little later than the other two sites, fairly dry conditions had prevailed prior to the sampling occasion at this site.

9 DISCUSSION

9.1 REFERENCE SOIL PROFILES

Soil reference sites were mainly located in the areas of low humic latosol. The Bagatelle site was possibly contaminated from previous settlements. This was shown in the results of zinc and organic content, which differed greatly from results from the other sites. As a result, the metal concentrations from Bagatelle were discarded and have not been part of the reference material.

Concentrations of copper, lead and zinc at the soil reference sites are well within the range for naturally occurring concentrations on earth described in Alloway (1995). When compared to findings by Sutherland and Tolosa et al. (2001) in Hawaii, total concentrations are lower for all metals (88 mg/kg compared to 115 mg/kg for Cu, 7 and 13 mg Pb/kg while corresponding figures for Zn were 67 and 141 mg/kg). The ranges for all metals were similar to background levels on Hawaii presented by Sutherland and Tolosa (2001). Deep soil samples in Table 5 can give an idea about the natural variation in concentration of metals in the reference soils. Keeping in mind that the number of reference samples is low, Cu exhibited the greatest natural variation in the collected samples, whereas Pb and Zn showed that naturally, concentrations do not vary to a great extent.

Bioavailable lead concentrations found in the upper soil layer at the selected reference sites were low (16-26 mg/kg) compared to the main sampling sites (up to 192 mg/kg), but even so they were at least 30 % greater than the concentrations found at a depth of 50 cm at the same sites. This implies that a large scale deposition of Pb is prevalent in Mauritius. Zinc does not differ when considering soil samples at different depths at the reference sites, hence it can be concluded that Zn has a lower degree of airborne particles than is the case for Pb. Bjelkås and Lindholm (1994) suggest that only 5 % of emission from tires, which is the greatest Zn contributor from traffic, contains particles small enough to be carried with the wind.

9.2 MAIN SOIL SAMPLING SITES

The ambition was to find sampling sites with the same soil type so that soil qualities would be similar. Redit is clearly within the soil type of low humic latosol, whereas Moka is in the border area of low humic latosols and mountain slope complexes. The soil at Camp Auguste consists of latosolic red prairie soil and looking at pH, possibly Camp Auguste was slightly more acidic than the other sites. Regarding organic content it was not possible to differentiate between the main sampling sites. However, grain size differed among the sites, which might have an impact on the metal concentrations. The grain size analysis revealed that the site of Moka had the greatest proportion in the silt and clay fraction (about 79 %), followed by Camp Auguste with 61 % whereas the Redit site had 42 % of its material finer than 63 µm.

Another factor that might have had an impact on the concentration of metals is the wind direction. The southeasterly trade winds that prevail for a great part of the year in Mauritius might have affected the distribution of emissions from the highway at the site of Redit, as it is situated in an open, flat area. If so, there will be a slight overestimation of the concentrations found at the distance from 3.5 to 22 m. However, the greatest concentrations were found in the samples that were nearest the road, located

further north. As this point is placed in a gentle downhill slope, it can be assumed that the slope effect levels off the wind effect at this particular point. The sampling sites of Moka and Camp Auguste are located in areas that are protected from the wind, so there should be very little interference of this sort.

9.2.1 Bioavailable and total concentrations

The metals investigated showed varying degrees of enrichment with distance from the roads that were part of the study. Concentrations of copper in the bioavailable fraction from the main sampling sites sometimes varied between individual samples, but no pattern was discernible. There was no indication on Cu contamination from vehicles as levels in both the top and lower soil layers were similar to those found at the reference sites, even at the depth of 50 cm. This implies that the detected Cu concentrations were of a natural origin rather than from emissions derived from traffic. Total concentrations of copper showed similar results as the bioavailable fraction. 45-73 % of the copper was found in the residual fraction and as ten out of twelve samples imply that more than 60 % of the total copper concentration was found in the crystalline structure, this points to the high natural occurrence of Cu. Since the occurrence of Cu seems to be mainly of natural origin, lead and zinc are the metals that will be discussed further in the following text.

The most elevated concentrations of bioavailable Pb and Zn were found in the close vicinity of the highway at Reduit, where the vehicle density was also the greatest. Single samples from the top soil layer at this site contained concentrations of Pb exceeding 200 mg/kg, but with distance the concentration decreased rather rapidly. At the distance of about 20 m, Pb values at Reduit were comparable to deep soil samples found at the reference sites. Compared to reference samples, Zn also exhibited elevated concentrations close to the highway at Reduit and even though the decrease with distance was evident, top soil samples collected farthest from the road at this site were slightly richer in Zn than the average background concentration.

The same pattern was discernible at Moka, but overall concentrations of Pb and Zn were smaller. As the probability for capturing contaminants in the bioavailable form generally increases with the amount of fine material, and assuming that the distribution of finer material at the sampling sites was the same, the greater Pb and Zn concentrations found at Reduit, as compared to Moka, can not be explained by geological factors but support the theory that they are a consequence of a heavier traffic load. The wind effect may possibly have affected sampling points at 3.3 m and further away at Reduit, but as the sampling points at 1.5 m were unaffected by this and still exhibited the greatest concentrations the impact from vehicles was apparent.

At Camp Auguste, Zn concentrations were relatively constant along the transect and levels in all samples but the ones at 20 m distance may be interpreted as somewhat greater than background levels. Pb levels were slightly greater than background values along the transect, however there was a peak of lead at the distance of about 3 m from the road, which could be assigned the deviation problem for this metal. But at the same point measured pH was very low, which suggests that the result is correct and that the sampling point may not have been representative for this distance.

Due to deviations in the analyses of lead, the results obtained in this study suggest that 0 to 61 % of the total lead concentration should be in the crystalline structure. Here, the

smaller percentage corresponds to the cases where total lead exceeded the bioavailable fraction according to the results. This was particularly true for small concentrations, e.g. for samples collected at Camp Auguste, and at the furthest sampling points at Reduit and Moka. The problem with great Pb variations in analyses is further discussed below. 37-88 % of zinc was found in the fraction that is not available for biota and it was evident that a greater amount of the total Zn was found in the close proximity to the highways at Reduit and Moka than further away from the roads, pointing to the pollution from roads.

Ratios

The enrichment of lead and zinc at the sites was even more apparent when considering the ratio of bioavailable metal concentrations in roadside soils and the mean metal concentrations from deep reference samples. It should be kept in mind that the ratio is not necessarily 1 when there is no enrichment. This is due to the fact that measured concentrations always display deviations to a certain extent. Samples with ratios less than 2 have been considered not having elevated concentrations.

Ratios of bioavailable lead and zinc concentrations in roadside soils and the average metal concentrations from deep reference samples (50 cm) are displayed in Figure 11 and 12. For a full listing of ratios, see Appendix 5. The enrichment of Pb and Zn at the sites was apparent. At Reduit the enrichment of bioavailable lead in the top soil layer close to the highway was about 19 times the concentration found in deeper soil samples at the reference sites. Enrichment of total Pb at the same point was 31 times the background level. The relatively narrow band of heavy contamination was evident as the ratios declined rapidly with distance. At Moka, where the traffic density was estimated at approximately half the density of Reduit, the ratios for bioavailable and total Pb in the upper 5 cm were calculated to 6 and 15 respectively, which seem reasonable in comparison. At a distance of about 20 m Pb levels were comparable to background levels for both Reduit and Moka. At Camp Auguste the sample at 3.3 m distance showed a ratio of 5, whereas the other samples at the site were around 2.

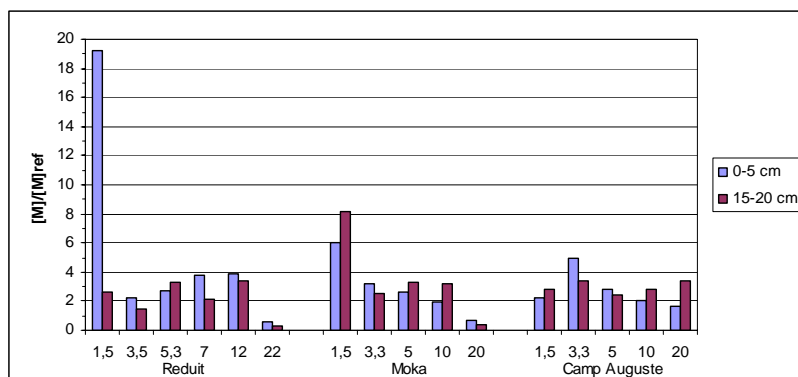


Figure 11 Ratios between bioavailable Pb in soil samples and average of bioavailable Pb in deep reference samples.

The ratios of zinc, shown in Figure 11, imply that there was an enrichment of zinc close to the highways at Reduit and Moka as compared to background levels. At Reduit, concentrations were greatly elevated up to a distance of 3.5 m, but only at 22 m did they decrease to background levels. The band of greater contamination appeared wider at

Moka, however at 10 m distance the Zn content was comparable to the deep reference samples. At Camp Auguste neither upper nor lower soil samples exhibited any elevated levels of Zn.

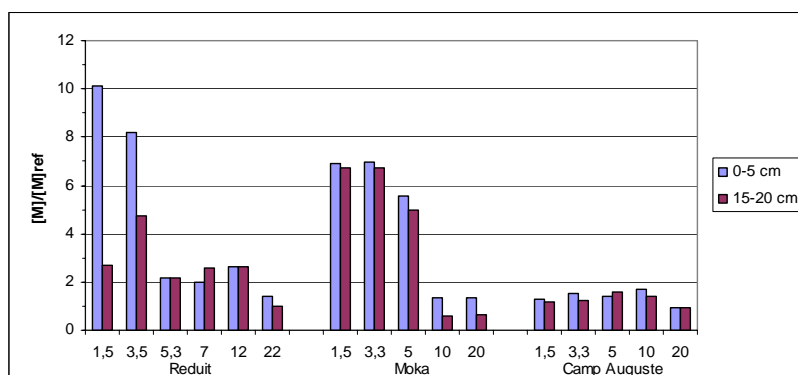


Figure 12 Ratios between bioavailable Zn in soil samples and average of bioavailable Zn in deep reference samples.

9.2.2 Easily soluble and exchangeable metals

The literature has suggested that total levels of copper, lead and zinc in the pore water are greater than detection limits for the F-AAS, but considering the great affinity of these metals for charged surfaces and organic matter in soils, it is not surprising that concentrations of metals found in the extraction for easily soluble and exchangeable metals were small. In addition, the heavy rainfall prior to the days of sampling (see Appendix 4) might have had an impact on the metals' presence in the soil solution, though this effect is probably very small compared to the influence from the strong binding of the metals in the soil.

9.2.3 Comparisons to other findings and calculations

As written previously, it has to be kept in mind that the values set by the Swedish EPA also include metals bound to insoluble Al-, Fe- and Mn-oxides and organic matter with complex matrices, which are not extracted when using HCl. Despite this disagreement, some conclusions can be drawn. No sample exceeded the guidance value set by the Swedish EPA regarding zinc (see Table 2), and it is not possible to say whether this is due to a real deviation between concentrations or if it is a result of the different methods being used. Despite the different methods, it is safe to say that where concentrations from this study exceed the values set by the Swedish EPA there is a risk to human health and/or environment. The copper value was occasionally exceeded, though this can probably be explained by the differences in soil composition between Mauritius and Sweden. Lead, on the other hand, is not naturally abundant in great portions in either of the soil types, but nonetheless the guideline value was exceeded in the close proximity to highways at Redit and Moka, which yet again points to the pollution from traffic.

When weighing lead results from this study against previous ones, it was apparent that the total concentrations of lead were lower than those of Naga (1998) and Veerappapillay (2000). However, sampling points closest to the highways at Redit and Moka displayed concentrations within the range that were found at Grand Bay and Triolet prior to the introduction of unleaded petrol. Findings by Ranjeet (2000) were greater regarding copper, lead and zinc, though as the study focuses on the Bel-Village-Phoenix Trunk Road with sampling points closer to Port Louis where concentrations are

expected to be greater, this was not surprising. Also, these studies were all carried out prior to the introduction of unleaded petrol. Nonetheless, it is noteworthy that the results from year 2000 exhibits enhanced Cu concentrations in comparison to background levels found in this study, possibly implying that copper emissions might be important pollutants at greater traffic densities.

Calculations on the contribution of copper, lead and zinc from traffic were very high compared to measured concentrations. For example, at 5.3 m distance from Reduit the measured zinc level was 33 mg/kg. If all Zn emitted from vehicles would enter and stay in the upper 5 cm of the soil, this level would be reached within three years time. Regarding lead, about four years would be needed to reach measured concentrations at the same sampling point. At Moka, measured concentrations of Zn at the distance of 5 m were rather great and only after a little less than 20 years this level would be reached according to the calculations. For Pb about 13 years would be required to reach the measured levels. According to the information gathered and the calculations made, the contribution of traffic-related copper at Reduit and Moka is equal to the emitted amount of Pb. However, the sites did not exhibit any enhanced measured Cu concentrations. In estimating the release from highway traffic at Reduit and Moka, many assumptions had to be made and consequently there is a great uncertainty in the results. Also, one can expect that in a tropical climate, with intensive rainfall, a great portion of metals will not stay in the soil, since Cu and Pb in soil forms strong complexes with soluble humic and fulvic acids, which may be flushed away easily. However, this is in contrast to findings in Hawaii, where Teutsch et al. (1999) proposed that concentrations of Pb in soil increase with increasing rainfall, whereas Zn is depleted and Cu concentrations are constant.

9.3 SEDIMENT

Unfortunately, suitable sediment samples were difficult to find in the area. The aim was to locate accumulation zones where particulate matter from each respective road might have been deposited. However, such zones were only found at the dam and upstream from the sampling site of Reduit. Sediment samples collected at the sites were rather coarse and probably originated from erosion of the riversides in the very close vicinity, rather than from places further upstream in the system. Hence they should be seen as representative of only their particular sites and conclusions for the rest of water system should not be drawn. In the end, samples that would represent the contribution of metals to each respective river from road runoff were collected underneath the bridges. The visual difference in the amount of sediments at the sites between the days of field site identification (January) and the sampling occasions (February and March) could be noticed. In between these occasions, all rivers had experienced peaks of discharges, see Appendix 3. Considering the results on bioavailable metals, no trend can be distinguished, neither with distance from the road nor with time. There are slightly greater concentrations of Zn found at the bridge of Moka compared to other sediments samples. Copper is the only metal that exceeds the Swedish reference guidelines for contaminated surface sediments, though again this can be ascribed to the natural differences in soil rather than pollution from traffic.

In the study conducted by Gustavsson (2004), samples were collected in the estuary of Grand River North West catchment area and in the Black River estuary, which is considered little affected by anthropogenic activities and therefore was used as a reference. Gustavsson (2004) used a finer grain size for the analysis, hence

concentrations from that study can be expected to be somewhat greater even if the actual content of metal in the total samples would be the same in both studies. At all sites, measured copper concentrations were generally in the upper range of results obtained from Grand River North West, which seems difficult to explain as the sites are situated in the upper region of the same catchment area and soil types do not show a great diversity in the region. Measured concentrations of lead were greater than Black River but smaller than Grand River North West, which was expected. Compared to Grand River North West, concentrations of zinc at Reduit, Moka and Camp Auguste were much smaller, but as Black River mostly runs through a national park it was unexpected to find that most Zn levels were slightly lower than the ones from Black River. Possibly this difference can be attributed the difference in soil types between the areas. Also Gustavsson (2004) used the Swedish standard (7 M HNO₃) for evaluation of the sediment samples, hence comparisons are not completely in accordance.

9.4 INTERPRETATION DIFFICULTIES

Ideally the number of samples representing a sampling point is four, but it might be smaller than this due to sources of error. The majority of results for doubles and duplicates were quite scattered for all metals analysed, which can be seen in Appendix 2. When studying lead results, differences between individual samples sometimes reached a factor of 2, and in one case even a factor of 3. Regarding copper and zinc, differences between doubles and duplicates were generally less than a factor of 2, with the exception of samples collected at the site closest to the busiest road and the soil reference sample from Bagatelle. For duplicates, the variation was sometimes high too, but generally smaller than between doubles.

One factor affecting the results of a study like this is the homogeneity of each sample. Firstly, there might be substantial local variations at a specific site and samples collected from there might exhibit different metal concentrations. Secondly, the selected grain size for analysis may also have a great impact on the outcome. In this case, the grain size used for metal analyses was $\leq 425 \mu\text{m}$, in order to facilitate comparisons with previous results from Mauritius. Though, the larger the particle fraction to be analysed, the less homogenous the sample. Thus, where the same soil sample has been divided into different test tubes, metal concentrations detected are likely to show greater variations if coarse material is used as compared to soil comprising finer particles. These factors have probably been significant in the results from this study, contributing to the deviations.

For total lead, results showed fairly good consistency between the samples and, like copper and zinc, all individual results were included in the averages. On the contrary, bioavailable lead analyses for doubles and their duplicates displayed large deviations. The problem with great variability in lead concentrations in environmental studies has been highlighted previously. Assessments of traffic-related metals performed in, for example Sweden and Israel, points to the high variability of lead in topsoil (Vägverket, 1998; MFA, 2005). Tessier et al. (1979) and other workers have reported problems with low reproducibility of lead results in sediment samples.

Generally, sample solutions containing less than 0.1 mg Pb/l may not give stable results during F-AAS analyses (Påhlsson, personal communication, 2005) and therefore samples containing smaller concentrations than this (which equals 1.25 mg Pb/kg dw in this study) were discarded during the data processing. In many cases, this resulted in

few results to generate reliable averages of bioavailable lead. Subsequently, a second run of the samples by F-AAS was completed for this fraction. The time period between the first and second run of analyses, however, seems to have had an impact on the results when reading concentrations of bioavailable lead. In general all samples from the second run showed smaller concentrations of lead than the first run; consequently, the results from the later run were not used in the final evaluation of metal pollution, except where the first F-AAS run failed to contribute to an average. In some of the bottles where the extracted and digested samples were kept, solid particles were visible on the bottom after the second run. This might imply that precipitation of humic complexes may have occurred, hence lowering the concentration of lead in the solution.

9.5 IMPROVEMENTS

As there was no access to a soil sample standard, it was not feasible to investigate the possible influence of the soil matrix itself on metal concentrations in this project. Neither has a standard been used when analysing the sediment samples. Another way of identifying possible interferences from the soil matrix or losses by e.g. volatilization is to spike samples in the field, with a known amount of a certain element or compound (Förstner, 2004). As none of these techniques were used, there may have been interference from substances contained in the samples other than the actual metal analysed. Tessier et al. (1979) estimated this effect to contribute with roughly 15 %. Matrix interference, together with the above discussed deviations, give reason to treat the reported absolute concentrations in this project with some caution, although the obtained averages may give a hint about the present situation.

Pb and Zn exhibited enriched levels in the close proximity (<20 m) to the highways at Redit and Moka. Nonetheless, it should be emphasized that even though it is possible to point to enhanced Pb and Zn concentrations close to the roads at Redit and Moka, it has not been possible to prove this statistically. This is due to low accuracy throughout the analysis of the samples at each sampling point. Neither is it statistically established that concentrations differ between sampling sites or that the levels of metals in the upper layers are significantly greater than concentrations further down the soil profile. It would have been possible to collect a sufficient number of samples to work with statistically if another approach had been used, focusing on only one main sampling site. However, as this project aimed at also taking the factor of traffic density into account when quantifying the probable emission from vehicles, this was not feasible.

10 CONCLUSIONS

In the very proximity to highways at Redit and Moka, enhanced concentrations of lead and zinc were detected. Obtained levels correlated well to traffic densities. However, concentrations decreased rapidly with distance, and 20 m away levels were comparable to background levels.

Small concentrations of metals in the easily soluble and exchangeable fraction indicated that metal contribution from soil into the surface water or groundwater systems is not a great threat at the sites included in the study. This was also supported by the grain size analysis of the soils.

Cu displayed no trends in concentrations neither with distance from roads, nor with depth or with differences in traffic density, implying that levels found in this project represented natural background levels.

The results provide some background information on naturally-occurring copper, lead and zinc concentrations in soils in Mauritius, which may be useful for further studies of the environmental situation in the country. Also the results from the soil reference sites hinted to a large-scale low-level pollution of Pb in the country.

The importance of carrying out analysis as soon as possible after extraction or digestion, to prevent unwanted changes of the samples from occurring, must be stressed.

There was a tendency of high variability in Pb results, making interpretations of the metal difficult. The problem has been highlighted previously.

It was established that the band of heavier contamination along highways was relatively narrow (<20 m), and generally concentrations were smaller as compared to studies carried out previously in Mauritius. However, it is important to follow the development within the subject. From having lowered the content of lead in petrol it follows that the emission of the metal per km and vehicle decreases. Though since indications are strong that the number of vehicles in the country will continue to increase, it is likely that the burden of traffic-related heavy metals in soil and sediment in the road close environment will be greater in the future.

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APPENDIX 1: Soil Reference Sites

In order to quantify the contribution of metals from vehicles to the surrounding environment at the main sampling sites, soil references were collected at five sites which are described below. As climatic conditions change rather rapidly with short distances in Mauritius, they were all selected within the drainage area of Grand River North West, fairly close to the main sampling sites.

Bagatelle

Grass and low bushes cover this site which is located about 15 m from a little trafficked gravel road. Low humic latosol is the soil type here. Even if there are no buildings or remains left here today, this site seems to have been inhabited some time back. The soil was rather dark and the organic content was large compared to the other sites. Results from the F-AAS analyses pointed to the contamination of especially zinc. Possibly has this site been inhabited previously, affecting the natural concentrations of metals at this site.

Chebel

The open flat area of this site is covered with tall grass and the occasional bush. The soil is low humic latosol. Roads of any significance are further than 500 m away from where the samples were collected, hence providing a good site for background samples.

Le Pouce

This site is more than 300 m from any road, just at the foot to the mountain of Le Pouce. The vegetation is fairly tall, with grass and bushes. Soil type is low humic latosol but the site is close to the areas of mountain slope complexes. The site is within the catchment area of the Moka site.

Henrietta

Close by the residence area of Highlands, this area is covered mainly with not so dense bushes and the soil type is defined as latosolic red prairie soil according to the soil map (1962). Smaller roads are not too far off, but as they are assumed to host very low traffic densities, this site is still of interest as a reference site. The nearest main road is still quite small but within 300 m distance from this site.

Trianon

Situated close to the River Plaines Wilhelms, this site is an open area where the soil is labelled as low humic latosol. There is a small road at a distance of approximately 200 m which is sparsely used. Except for this the nearest bigger highway is the Bel Village-Phoenix Trunk Road about 700 m away.

APPENDIX 2 Results from chemical analyses

In the tables below, italic figures denote samples that have been neglected. These are:

- Cu and Zn concentrations smaller than detection limit (0.075 mg/kg), they are denoted 0 in the following tables and Pb concentrations smaller than 1.25 mg/kg.
- Some samples having a concentration 8 or 9 mg Pb/kg. The result list from the analysis indicated on errors in the extraction process or measuring errors.
- Bagatelle samples.

Bioavailable Cu in soil samples [mg/kg].

| Depth | 0-5 cm | | | 15-20 cm | | | 50 cm | | |
|------------------|-----------|-----------|-----------|-----------|-----------|-----------|-------|----|-----------|
| | 1 | 2 | Av | 1 | 2 | Av | 1 | 2 | Av |
| Reduit | | | | | | | | | |
| 1.5 m | 34 | 9 | 30 | 35 | 38 | 38 | | | |
| | 30 | 48 | | 36 | 41 | | | | |
| 3.5 m | 43 | 43 | 42 | 39 | | 24 | | | |
| | 39 | 44 | | 10 | | | | | |
| 5.3 m | 34 | 39 | 37 | 36 | 36 | 27 | | | |
| | 39 | | | 9 | 9 | | | | |
| 7 m | 39 | 20 | 35 | 40 | 39 | 28 | | | |
| | 40 | 40 | | 8 | 25 | | | | |
| 12 m | 39 | 38 | 39 | 39 | | 39 | | | |
| | 39 | | | 40 | 40 | | | | |
| 22 m | 30 | 28 | 28 | 29 | 30 | 29 | | | |
| | 32 | 20 | | 31 | 25 | | | | |
| Moka | | | | | | | | | |
| 1.5 m | 38 | 36 | 44 | 42 | 35 | 40 | | | |
| | 39 | 62 | | 46 | 36 | | | | |
| 3.3 m | 35 | 33 | 34 | 39 | 37 | 38 | | | |
| | 34 | 34 | | 39 | 36 | | | | |
| 5 m | 32 | 33 | 32 | 38 | 39 | 38 | | | |
| | 32 | 31 | | 43 | 32 | | | | |
| 10 m | 36 | 36 | 34 | 35 | 35 | 34 | | | |
| | 39 | 25 | | 34 | 34 | | | | |
| 20 m | 34 | 33 | 37 | 37 | 39 | 39 | | | |
| | 41 | 38 | | 40 | 40 | | | | |
| C Aug | | | | | | | | | |
| 1.5 m | 30 | 28 | 30 | 29 | 29 | 30 | | | |
| | 31 | 32 | | 30 | 30 | | | | |
| 3.3 m | 29 | 30 | 28 | 28 | 30 | 21 | | | |
| | 27 | 26 | | 15 | 11 | | | | |
| 5 m | 29 | 29 | 27 | 29 | 29 | 29 | | | |
| | 28 | 24 | | 30 | 28 | | | | |
| 10 m | 31 | | 29 | 43 | 29 | 32 | | | |
| | 28 | | | 28 | 28 | | | | |
| 20 m | 32 | 30 | 29 | 29 | 31 | 30 | | | |
| | 32 | 22 | | | 31 | | | | |
| Bagatelle | <i>10</i> | <i>37</i> | 26 | <i>7</i> | <i>31</i> | 26 | | | |
| | <i>30</i> | <i>28</i> | | <i>10</i> | <i>72</i> | | | | |
| Chebel | 25 | 27 | 26 | 30 | 25 | 26 | | | |
| | 26 | 27 | | 25 | 25 | | | | |
| Henrietta | 17 | 20 | 17 | 16 | 15 | 17 | 33 | 41 | 41 |
| | 10 | 20 | | 19 | 17 | | 44 | 45 | |
| Le Pouce | 41 | 34 | 36 | 30 | 27 | 29 | 20 | 18 | 20 |
| | 36 | 36 | | 29 | 30 | | 21 | 18 | |
| Trianon | 33 | 31 | 32 | 29 | 32 | 31 | 24 | 40 | 34 |
| | 32 | 31 | | 29 | 32 | | 36 | 37 | |

Bioavailable Pb in soil samples [mg/kg].

| Depth | 0-5 cm | | | 15-20 cm | | | 50 cm | | |
|------------------|--------|-----|------------|----------|-----|-----------|-------|----|-----------|
| | 1 | 2 | Av | 1 | 2 | Av | 1 | 2 | Av |
| Reduit | | | | | | | | | |
| 1.5 m | 256 | 158 | 192 | 39 | 14 | 26 | | | |
| | 202 | 153 | | 36 | 16 | | | | |
| 3.5 m | 20 | 22 | 23 | 19 | | 14 | | | |
| | 6 | 43 | | 10 | | | | | |
| 5.3 m | 26 | 8 | 27 | 9 | 33 | 33 | | | |
| | 29 | | | 9 | | | | | |
| 7 m | 40 | 27 | 37 | 42 | 32 | 22 | | | |
| | 45 | 9 | | 6 | 6 | | | | |
| 12 m | 39 | 9 | 39 | 85 | | 34 | | | |
| | 9 | | | 9 | 9 | | | | |
| 22 m | 9 | 6 | 6 | 3 | 0 | 3 | | | |
| | 3 | 0 | | 0 | 3 | | | | |
| Moka | | | | | | | | | |
| 1.5 m | 81 | 76 | 61 | 105 | 94 | 82 | | | |
| | 13 | 72 | | 41 | 87 | | | | |
| 3.3 m | 25 | 39 | 32 | 20 | 31 | 25 | | | |
| | 9 | 9 | | 9 | 9 | | | | |
| 5 m | 24 | 20 | 27 | 33 | 0 | 33 | | | |
| | 9 | 36 | | 9 | 32 | | | | |
| 10 m | 19 | 20 | 19 | 44 | 21 | 32 | | | |
| | 8 | 0 | | 9 | 9 | | | | |
| 20 m | 7 | 0 | 7 | 4* | 0 | 4 | | | |
| | 9 | 0 | | 5* | 0 | | | | |
| C Aug | | | | | | | | | |
| 1.5 m | 23 | 21 | 22 | 25 | 24 | 28 | | | |
| | 21 | 24 | | 32 | 32 | | | | |
| 3.3 m | 49 | 43 | 49 | 31 | 43 | 34 | | | |
| | 55 | 1 | | 28 | 0 | | | | |
| 5 m | 34 | 31 | 28 | 18 | 38 | 24 | | | |
| | 20 | 1 | | 20 | 20 | | | | |
| 10 m | 22 | | 21 | 28 | 37 | 28 | | | |
| | 20 | | | 37 | 11 | | | | |
| 20 m | 32 | 13 | 17 | 1 | 40 | 34 | | | |
| | 5 | 0 | | | 29 | | | | |
| Bagatelle | 41 | 28 | 28 | 26 | 7 | 69 | | | |
| | 40 | 2 | | 0 | 174 | | | | |
| Chebel | 14 | 10 | 12 | 9 | 9 | 7 | | | |
| | 15 | 10 | | 9 | 7 | | | | |
| Henrietta | 26 | 27 | 26 | 55 | 58 | 41 | 10 | 9 | 10 |
| | 0 | 0 | | 2 | 50 | | 10 | 9 | |
| Le Pouce | 23 | 31 | 16 | 24 | 30 | 33 | 10 | 7 | 9 |
| | 4 | 6 | | 33 | 47 | | 10 | 10 | |
| Trianon | 28 | 39 | 16 | 28 | 55 | 33 | 14 | 11 | 12 |
| | 0 | 0 | | 26 | 26 | | 15 | 10 | |

* concentrations from 2nd run of analysis

Bioavailable Zn in soil samples [mg/kg].

| Depth | 0-5 cm | | | 15-20 cm | | | 50 cm | | |
|------------------|------------|------------|------------|------------|----------|------------|-------|----|-----------|
| | 1 | 2 | Av | 1 | 2 | Av | 1 | 2 | Av |
| Reduit | | | | | | | | | |
| 1.5 m | 175 | 120 | 152 | 33 | 47 | 40 | | | |
| | 195 | 116 | | 35 | 47 | | | | |
| 3.5 m | 76 | 166 | 123 | | 64 | 71 | | | |
| | 74 | 175 | | | 79 | | | | |
| 5.3 m | 19 | 35 | 33 | 36 | 32 | 33 | | | |
| | 44 | | | 30 | | | | | |
| 7 m | 44 | 5 | 30 | 48 | 38 | 38 | | | |
| | 43 | 28 | | 37 | 30 | | | | |
| 12 m | 43 | 36 | 40 | 38 | 46 | 39 | | | |
| | 40 | | | | 33 | | | | |
| 22 m | 15 | 16 | 21 | 15 | 12 | 15 | | | |
| | 28 | 25 | | 13 | | | | | |
| Moka | | | | | 20 | | | | |
| 1.5 m | 94 | 102 | 103 | 97 | 97 | 101 | | | |
| | 104 | 113 | | 102 | 107 | | | | |
| 3.3 m | 115 | 107 | 105 | 104 | 114 | 101 | | | |
| | 100 | 97 | | 84 | 101 | | | | |
| 5 m | 89 | 90 | 84 | 81 | 79 | 74 | | | |
| | 74 | 82 | | 66 | 72 | | | | |
| 10 m | 15 | 20 | 20 | 12 | 14 | 9 | | | |
| | 35 | 11 | | 5 | 3 | | | | |
| 20 m | 19 | 0 | 20 | 9 | 7 | 10 | | | |
| | 26 | 15 | | 12 | 11 | | | | |
| C Aug | | | | | | | | | |
| 1.5 m | 21 | 15 | 20 | 15 | 19 | 18 | | | |
| | 26 | 17 | | 13 | 23 | | | | |
| 3.3 m | 20 | 29 | 23 | 29 | 17 | 18 | | | |
| | 20 | 23 | | 23 | 4 | | | | |
| 5 m | 21 | 25 | 21 | 21 | 26 | 24 | | | |
| | 20 | 17 | | 22 | 25 | | | | |
| 10 m | 27 | | 26 | 23 | 21 | 21 | | | |
| | 24 | | | 23 | 18 | | | | |
| 20 m | 16 | 7 | 14 | 15 | 11 | 14 | | | |
| | 16 | 16 | | 15 | | | | | |
| Bagatelle | <i>103</i> | <i>61</i> | 97 | <i>104</i> | <i>0</i> | 154 | | | |
| | <i>117</i> | <i>105</i> | | <i>204</i> | <i>0</i> | | | | |
| Chebel | 28 | 27 | 27 | 21 | 19 | 20 | | | |
| | 28 | 26 | | 20 | 18 | | | | |
| Henrietta | 5 | 5 | 5 | 0 | 0 | 0 | 6 | 16 | 14 |
| | 4 | 0 | | 0 | 0 | | 16 | 17 | |
| Le Pouce | 11 | 4 | 8 | 0 | 6 | 6 | 0 | 0 | 0 |
| | 9 | 10 | | 2 | 0 | | 0 | 0 | |
| Trianon | 21 | 15 | 15 | 8 | 10 | 10 | 18 | 16 | 16 |
| | 14 | 11 | | 12 | 9 | | 17 | 15 | |

Bioavailable metals in sediments [mg/kg].

| | Cu [mg/kg] | | | Pb [mg/kg] | | | Zn [ng/kg] | | |
|--------------|------------|----|-----------|------------|----|-----------|------------|----|------------|
| | 1 | 2 | Av | 1 | 2 | Av | 1 | 2 | Av |
| Redit | | | | | | | | | |
| Upstream | 280 | 28 | 28 | 47 | 19 | 16 | 61 | 36 | 34 |
| | 279 | 28 | | 34 | 13 | | 60 | 31 | |
| Dam 1 | 26 | 26 | 25 | 16 | 14 | 16 | 30 | 32 | 32 |
| | 25 | 25 | | 18 | 14 | | 34 | 31 | |
| Dam 2 | 31 | 34 | 29 | 16 | 14 | 13 | 33 | 43 | 38 |
| | 18 | 34 | | 7 | 15 | | 0 | 40 | |
| Bridge 1 | 27 | | 28 | 19 | | 25 | 30 | | 31 |
| | 28 | | | 30 | | | 32 | | |
| Bridge 2 | 31 | 39 | 34 | 16 | 9 | 16 | 34 | 37 | 36 |
| | | 33 | | | 9 | | | 36 | |
| Moka | | | | | | | | | |
| Upstream | 23 | 30 | 27 | 35 | 30 | 30 | 33 | 35 | 36 |
| | 25 | 31 | | 25 | 9 | | 39 | 36 | |
| Bridge 1 | 39 | 38 | 39 | 72 | 51 | 50 | 70 | 63 | 66 |
| | 37 | 40 | | 36 | 38 | | 66 | 64 | |
| Bridge 2 | 31 | 38 | 33 | 9 | 24 | 24 | 98 | 94 | 104 |
| | 30 | | | 9 | | | 118 | | |
| Downstream | 28 | | 29 | 1 | | 15 | 17 | | 36 |
| | 29 | | | 15 | | | 55 | | |
| C Aug | | | | | | | | | |
| Bridge 1 | 30 | 33 | 30 | 15 | 16 | 15 | 28 | 26 | 26 |
| | 27 | 32 | | 14 | 14 | | 30 | 23 | |
| Bridge 2 | 25 | 30 | 27 | 9 | 15 | 11 | 23 | 27 | 23 |
| | | 27 | | 11 | 12 | | 19 | 24 | |

Total Cu in soil samples [mg/kg].

| Depth | 0-5 cm | | | 15-20 cm | | |
|---------------|--------|-----|------------|----------|-----|------------|
| | 1 | 2 | Av | 1 | 2 | Av |
| Reduit | | | | | | |
| 1.5 m | 89 | 95 | 96 | 94 | 100 | 100 |
| | 94 | 107 | | 96 | 108 | |
| 22 m | 98 | 103 | 101 | 109 | 95 | 105 |
| | 106 | 96 | | 112 | 102 | |
| Moka | | | | | | |
| 1.5 m | 71 | 83 | 79 | 74 | 83 | 77 |
| | 85 | 79 | | 68 | 82 | |
| 20 m | | 102 | 100 | 104 | 101 | 101 |
| | | 98 | | 100 | 101 | |
| C Aug | | | | | | |
| 1.5 m | 77 | 90 | 82 | 80 | 79 | 83 |
| | 82 | 80 | | 83 | 88 | |
| 20 m | 84 | 90 | 84 | 79 | 89 | 85 |
| | 84 | 80 | | 83 | 88 | |

Total Pb in soil samples [mg/kg].

| Depth | 0-5 cm | | | 15-20 cm | | |
|---------------|--------|-----|------------|----------|-----|------------|
| | 1 | 2 | Av | 1 | 2 | Av |
| Reduit | | | | | | |
| 1.5 m | 285 | 159 | 220 | 34 | 13 | 24 |
| | 274 | 162 | | 36 | 13 | |
| 22 m | 8 | 13 | 12 | 8 | 8 | 8 |
| | 15 | 13 | | 6 | 11 | |
| Moka | | | | | | |
| 1.5 m | 106 | 101 | 103 | 110 | 118 | 109 |
| | 101 | 106 | | 93 | 116 | |
| 20 m | | 8 | 7 | 8 | 8 | 8 |
| | | 6 | | 8 | 8 | |
| C Aug | | | | | | |
| 1.5 m | 21 | 17 | 19 | 24 | 19 | 20 |
| | 19 | 19 | | 24 | 15 | |
| 20 m | 17 | 17 | 16 | 8 | 28 | 20 |
| | 17 | 15 | | 13 | 30 | |

Total Zn in soil samples [mg/kg].

| Depth | 0-5 cm | | | 15-20 cm | | |
|---------------|--------|-----|------------|----------|-----|------------|
| | 1 | 2 | Av | 1 | 2 | Av |
| Reduit | | | | | | |
| 1.5 m | 281 | 189 | 240 | 115 | 93 | 107 |
| | 282 | 208 | | 120 | 101 | |
| 22 m | 132 | 136 | 127 | 132 | 110 | 125 |
| | 117 | 124 | | 135 | 123 | |
| Moka | | | | | | |
| 1.5 m | 179 | 193 | 186 | 183 | 193 | 185 |
| | 187 | 185 | | 172 | 193 | |
| 20 m | | 65 | 64 | 71 | 72 | 71 |
| | | 62 | | 68 | 73 | |
| C Aug | | | | | | |
| 1.5 m | 99 | 104 | 100 | 83 | 85 | 89 |
| | 109 | 89 | | 92 | 96 | |
| 20 m | 81 | 76 | 75 | 65 | 86 | 73 |
| | 78 | 66 | | 59 | 82 | |

Total metals found at a depth of 50 cm at soil reference sites.

| | Cu [mg/kg] | | | Pb [mg/kg] | | | Zn [mg/kg] | | |
|------------------|------------|-----|-----------|------------|---|----------|------------|----|-----------|
| | 1 | 2 | Av | 1 | 2 | Av | 1 | 2 | Av |
| Henrietta | 88 | 101 | 96 | 6 | 6 | 6 | 53 | 48 | 74 |
| | 89 | 106 | | 6 | 4 | | 57 | 51 | |
| Le Pouce | 76 | 66 | 73 | 4 | 6 | 6 | 72 | 74 | 52 |
| | 81 | 69 | | 6 | 8 | | 72 | 79 | |
| Trianon | 80 | 106 | 94 | 11 | 8 | 9 | 74 | 69 | 74 |
| | 85 | 105 | | 13 | 4 | | 82 | 72 | |

The amounts of total metal that can be expected to be in the residual form were calculated as:

$$M_{residual} = \frac{[M_{total} - M_{bioavailable}]}{M_{total}}$$

Negative values were obtained where concentrations of total and bioavailable metals did not differ a lot.

| | Distance from road [m] | % Cu in residual form | | % Pb in residual form | | % Zn in residual form | |
|---------------|------------------------|-----------------------|----|-----------------------|-----|-----------------------|----|
| | | U | L | U | L | U | L |
| Reduit | 1.5 m | 69 | 63 | 13 | -8 | 37 | 68 |
| | 20 m | 73 | 73 | 49 | 61 | 81 | 88 |
| Moka | 1.5 m | 45 | 48 | 52 | 13 | 44 | 46 |
| | 22 m | 63 | 61 | -39 | 48 | 69 | 86 |
| C Aug | 1.5 m | 63 | 64 | -38 | -39 | 80 | 76 |
| | 20 m | 66 | 64 | -38 | -75 | 85 | 81 |

APPENDIX 3: Discharges

WRU provided data on daily discharge from the gauging stations at Moka and Cascades Rivers (station numbers W10 and W05 according to their system). The site for the discharge measurements on River Cascades is situated close (about 15 m) to the highway that crosses the country and along which the sampling site of Redit is located (see description in Chapter 6.1). The discharge given from these readings is equivalent to the discharge in the river at the site that will be affected by the highway. In order to estimate the discharge further upstream at the sampling site of Camp Auguste, the assumption was made that the specific runoff does not change within the drainage area of point W05. This is fairly reasonable considering that factors such as climate and slope do not change considerably within the drainage areas. There are no major tributaries in between the two points, however some streams enter the river and therefore the calculated discharges at Camp Auguste might be slightly underestimated. Though, rather than the absolute figures, the relative magnitude of discharge was desirable. Discharge at Camp Auguste was calculated as:

$$Q = \frac{Q^*}{A^*} \cdot A$$

Q = desired discharge

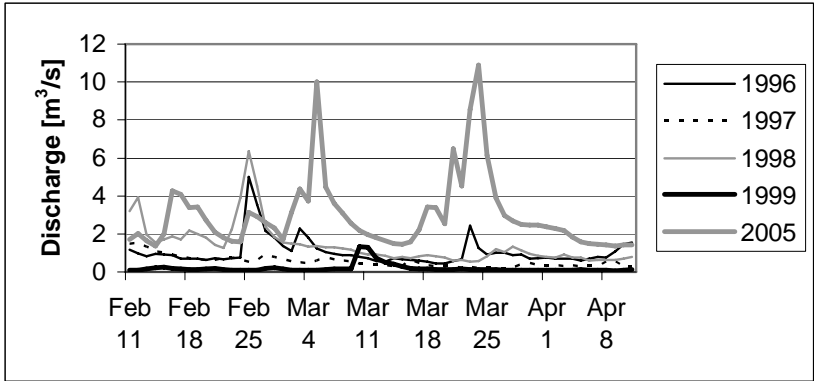
A = drainage area of point subject for calculation

Q^* = discharge at known gauging station

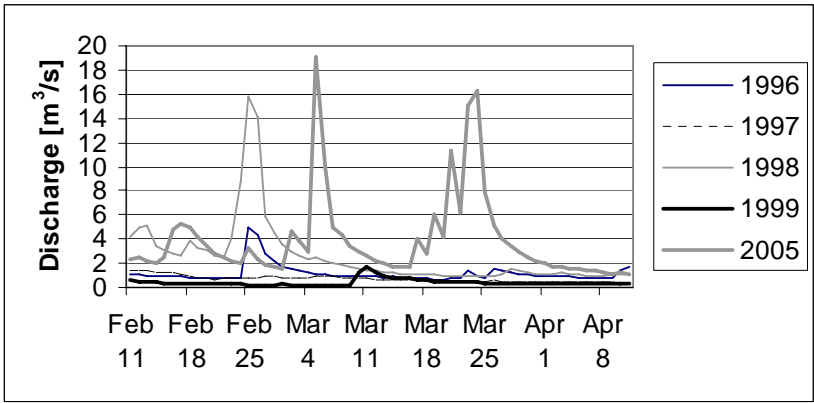
A^* = drainage area of point with known discharge

In River Moka the gauging station W10 is located upstream of the sampling site Moka and to get a rough figure of the discharge at the site where sediment sampling was carried out, a similar estimation as above was performed. In this case however, the estimation of the discharge at Moka sampling site will be somewhat larger than in reality as some minor tributaries enter the river downstream the gauging station but before the sampling site.

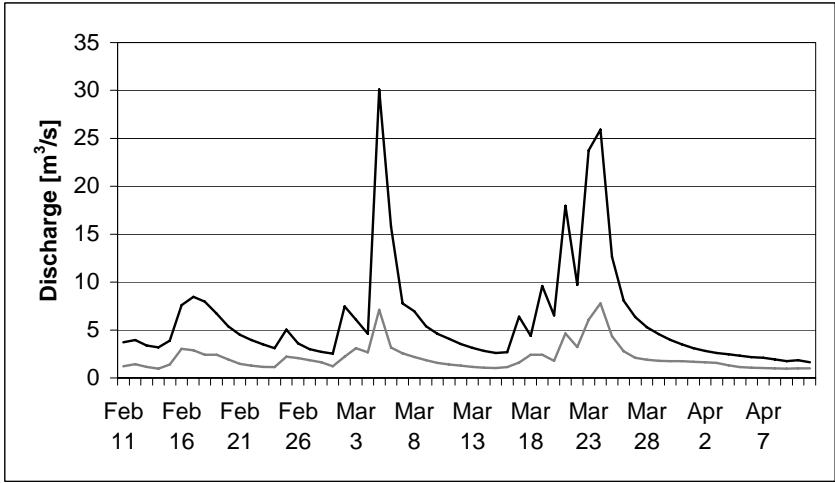
Discharges in rivers at sampling sites during time of sampling are displayed on the following page.



Measured daily average discharge in River Cascade at gauging station W05 (WRU) close to the sampling site of Reduit, and upstream the site of Camp Auguste.



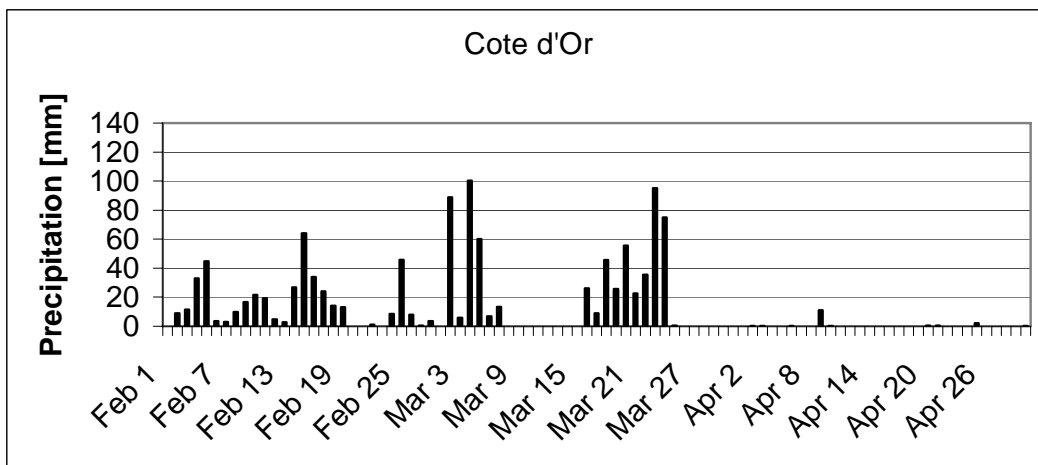
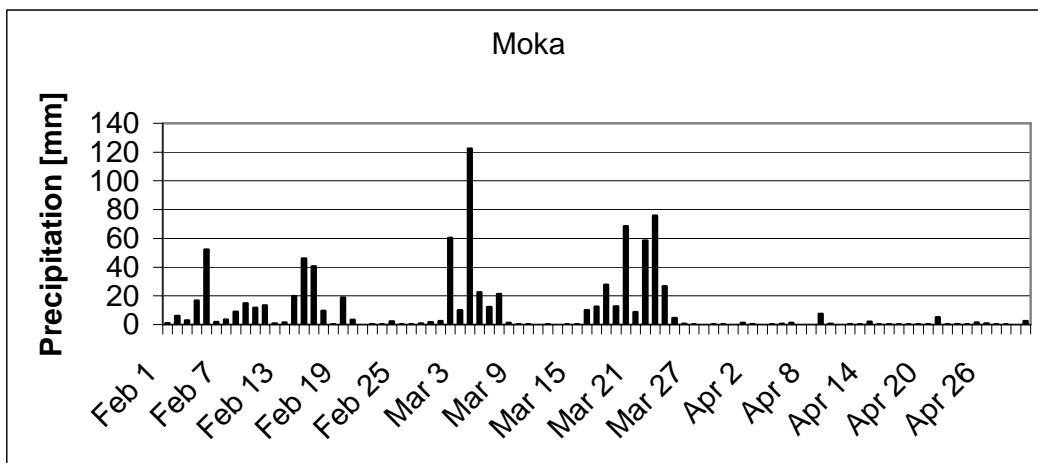
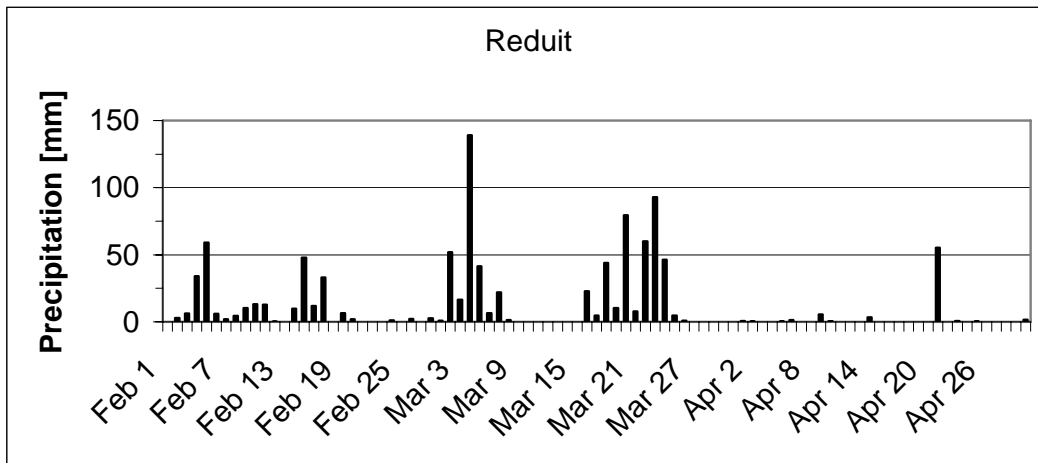
Measured daily discharge at gauging station in River Moka (Station W10, WRU), upstream the sampling site of Moka.



Calculated daily average discharges at the sampling sites Moka (black line) and Camp Auguste (grey line).

APPENDIX 4: Precipitation

Precipitation during the period of sampling at each main sampling site. Cote d'Or is the weather station that is next to Camp Auguste. Sampling date at Redit was February 21st, Moka February 18th and samples from Camp Auguste were collected March 17th.



APPENDIX 5: Ratios

Ratios between main sampling sites and reference sites for bioavailable and total metals.

| Dist. from road [m] | Cu | | | | Pb | | | | Zn | | | |
|---------------------|-----------|---|-------|---|-----------|---|-------|----|-----------|---|-------|---|
| | Bioavail. | | Total | | Bioavail. | | Total | | Bioavail. | | Total | |
| | U | L | U | L | U | L | U | L | U | L | U | L |
| Redit | | | | | | | | | | | | |
| 1.5 | 1 | 1 | 1 | 1 | 19 | 3 | 31 | 3 | 10 | 3 | 4 | 2 |
| 3.5 | 1 | 1 | | | 2 | 1 | | | 8 | 5 | | |
| 5.3 | 1 | 1 | | | 3 | 3 | | | 2 | 2 | | |
| 7 | 1 | 1 | | | 4 | 2 | | | 2 | 3 | | |
| 12 | 1 | 1 | | | 4 | 3 | | | 3 | 3 | | |
| 22 | 1 | 1 | 1 | 1 | 1 | 0 | 2 | 1 | 1 | 1 | 2 | 2 |
| Moka | | | | | | | | | | | | |
| 1.5 | 1 | 1 | 1 | 1 | 6 | 8 | 15 | 16 | 7 | 7 | 3 | 3 |
| 3.3 | 1 | 1 | | | 3 | 3 | | | 7 | 7 | | |
| 5 | 1 | 1 | | | 3 | 3 | | | 6 | 5 | | |
| 10 | 1 | 1 | | | 2 | 3 | | | 1 | 1 | | |
| 20 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 1 | 1 | 1 | 1 | 1 |
| C Aug | | | | | | | | | | | | |
| 1.5 | 1 | 1 | 1 | 1 | 2 | 3 | 3 | 3 | 1 | 1 | 1 | 1 |
| 3.3 | 1 | 1 | | | 5 | 3 | | | 2 | 1 | | |
| 5 | 1 | 1 | | | 3 | 2 | | | 1 | 2 | | |
| 10 | 1 | 1 | | | 2 | 3 | | | 2 | 1 | | |
| 20 | 1 | 1 | 1 | 1 | 2 | 3 | 2 | 3 | 1 | 1 | 1 | 1 |