Copper poisoning in wild ruminants in the Kruger National Park: Geobotanical and environmental investigation

D.G. GROBLER

Conservation Development, Kruger National Park, Private Bag X402, Skukuza, 1350 South Africa, and Department of Pharmacology and Toxicology, Faculty of Veterinary Science, University of Pretoria, Private Bag X4, Onderstepoort, 0110 South Africa

ABSTRACT

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A geobotanical and environmental investigation was undertaken to investigate the potential for copper poisoning in wild ruminants within the Phalaborwa area in the Kruger National Park and to confirm that environmental copper pollution associated with smelting operations at a nearby mine was the source of copper responsible for the poisoning. The study area selected was divided into high, moderate and low-risk zones and a control area based on initial topsoil copper concentrations and impala (*Aepyceros melampus*) liver copper concentrations in relation to distance from the copper smelter. Samples collected revealed that topsoil copper concentrations were significantly higher than subsoil copper concentrations at the same sites. There was a significant linear decrease in topsoil to subsoil copper concentration relative to distance from the copper smelter and thus from the high-risk zone to the control area. Copper concentrations of unwashed plant material were significantly higher than washed plant material at the same sites, indicating the deposition of copper on the plant surfaces. Copper deposits in dust fall buckets were significantly higher downwind than upwind from the smelter stack and the presence of atmospheric copper was also confirmed with the aid of low-volume air sampling monitors. The investigation confirmed that the emissions from the copper smelter were sufficient in amount and appropriate in direction to have contributed significantly to the topsoil copper concentrations, unwashed plant copper concentrations and dust fall results.

Keywords: *Aepyceros melampus*, air pollution, chronic poisoning, copper, impala, Kruger National Park, mining, wild ruminant

INTRODUCTION

The pollution of ecosystems and the environment with copper following mining activities has been thoroughly investigated and studied. Very early historic smelting activities caused severe devastation and permanent damage to plant communities, soil microflora and aquatic life (Hutchinson 1979). Mining activities indicate the presence of geochemical anomalies and local enrichment of a metal or metals. Therefore, soils surrounding a mining complex are likely to have above average concentrations of such a metal or metals. The concentration of a metal, such as copper, is largely dependent upon the copper content of the parent rock and environmental factors such as drainage, pH and the amount of organic matter present. The distinction between naturally occurring copper and anthropogenic copper requires careful statistical analyses of concentration profiles in soil and vegetation (Davies & Bennett 1985). Environmental contamination by copper, derived from industrial activity, is likely to be detected as surface deposits on soils and vegetation. Low-growing grasses generally have the highest, and tree foliage the lowest, concentrations of copper (Wild 1968). Naturally occurring copper may be assessed by measuring copper concentrations in soils deeper beneath the surface, and in carefully washed vegetation samples (Hutchinson 1979; Parada, Gonzales & Bergqvist 1987).

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The copper concentrations in plants vary widely but usually range from 1–50 ppm dry matter (DM) (Davies & Bennett 1985). Copper toxicosis of plants rarely occurs when they are grown under natural soil conditions, but it may occur in areas where soil has received significant anthropogenic copper inputs. Certain plant species, such as lichens and mosses, are especially sensitive to copper. High copper concentrations in soil may cause the elimination of sensitive plant species and selection for resistant ones, thereby changing the community composition and species diversity (Hutchinson 1979). Some plants have evolved mechanisms that enable them to tolerate high copper concentrations (Reilly, Rowel & Stone 1970), while others can accumulate copper (Wild 1968). The route of copper absorption appears to be from the soil rather than from direct atmospheric deposition, since copper is unlikely to be transported across leaf cuticles (Hutchinson 1979).

Total copper concentrations in soils are not necessarily indicative of the amount of copper that may be available to plants for absorption via their roots. In addition to measurement of total copper content, determinations of water soluble or available copper were also performed in a previous study (Hutchinson 1979). Retarded growth occurred in plants grown on copper contaminated soils near smelters, but their growth improved following the addition of lime, presumably because a higher soil pH decreases metal solubility and absorption. Only 3% of copper were water-extractable at a pH of 4,5, but the mobilization improved at a pH of 2,8 (Hutchinson 1979).

The effects of copper contamination on aquatic systems have also been thoroughly investigated. Normal copper concentration in surface water varies considerably, ranging from 0,5–1 000 mg/ℓ, with a median of 10 µg/ℓ (Davies & Bennett 1985), and in seawater, from 1–5 µg/ℓ (Piscator 1979). Copper pollution causes the elimination of certain sensitive aquatic species such as daphnids, scuds, midges and snails, which are important food organisms for fish, resulting in decreased numbers of fish. Elevated copper concentrations in water may also be directly toxic to fish, resulting in the elimination of certain fish species in natural lakes (Hutchinson 1979). The aquatic fate and transport of copper depends on the pH of water, its redox potential and the availability of other ions, ligands or sorbents present in water. Most of the copper in water will accumulate in the sediment of such an aquatic system (Hutchinson 1979). No reports could be found in which polluted water is incriminated as the primary cause of chronic copper poisoning in herbivores.

With the exceptions of copper smelting units, mines and processing plants where the immediate areas in the vicinity are affected, inputs of copper into the atmosphere are not large enough to cause substantial ecological effects (Cant & Legendre 1982). Average concentrations of copper in the atmosphere range from 5–50 ng/m^3 in rural areas and 30–200 ng/m^3 in urban locations, while levels of 2 000–9 500 ng/m^3 have been measured close to copper smelters (Davies & Bennett 1985). Contamination of soil and vegetation by air-borne copper and copper dust in the vicinity of copper mining and refining operations can pollute and affect and kill domestic livestock (Parada *et al.* 1987). During 1989 chronic copper poisoning and associated mortality was reported in cattle in the vicinity of the town of Phalaborwa, which is situated in the Northern Province, South Africa (Gummow, Botha, Basson & Bastianello 1991). Geobotanical and dust fall bucket data, as well as circumstantial evidence, implicated a copper smelting unit of a nearby copper mine as the most likely source of copper responsible for the poisoning.

An initial investigation in the Kruger National Park (KNP), which borders the copper mining complex, was conducted shortly after the cattle poisoning had been diagnosed (Gummow *et al.* 1991; Grobler 1996). Significantly higher ($P \leq 0,05$) copper concentrations in liver samples collected from buffalo (*Syncerus caffer*) and impala (*Aepyceros melampus*) culled in the Phalaborwa region of the KNP compared to buffalo and impala culled elsewhere in the KNP, were detected. Two impala deaths investigated during the same time, were ascribed to chronic copper poisoning based on post mortem evidence (Grobler 1996) and the results of copper analyses of their livers and kidneys (Gummow *et al.* 1991).

The KNP comprises 19 485 km^2 (1 948 528 ha) of savanna and bush country and is situated on the northeastern borders of the Northern and Mpumalanga Provinces of South Africa (Gertenbach 1983). The Phalaborwa region is located on the northwestern boundary of the park, north of the Olifants River, and south of the Letaba River (Fig. 1). Copper mining in this region dates back more than a thousand years, but modern mining activities commenced in the 1930s when phosphates and vermiculate were actively mined (Frick 1986). Palabora Mining Company Limited (PMC) was founded in 1956 to prospect the copper deposit. Following initial exploration activities and feasibility studies, pre-production mining operations commenced in September 1964, ore milling in December 1965 and copper smelting in 1966. Copper refining and casting was introduced in 1968 (Kuschke & Tonking 1971) and currently more than 350 000 tons of copper are produced per annum.

Particulates generated in the smelting process are removed from gas streams by high efficiency electrostatic precipitators (ESP) and wet scrubbing (Palabora Mining Company Limited 1990). The ESP replaced an older, less efficient precipitator in mid 1989. However, during the installation of the ESP, a process that lasted for 2 months, particulate matter were only removed by the scrubbing process, without any

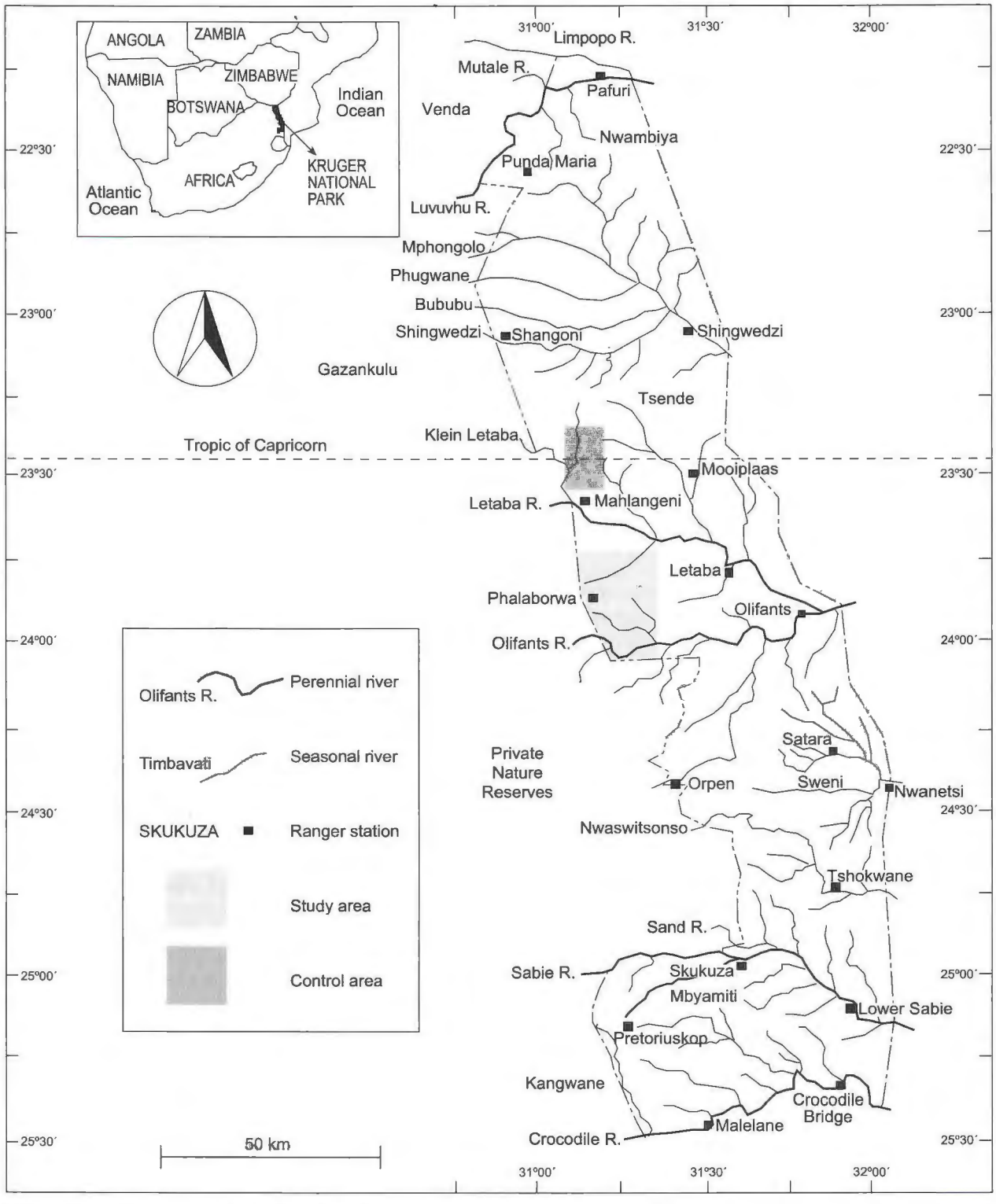

FIG. 1 Map of the Kruger National Park, South Africa, indicating study and contol areas

reduction in the output of the smelting operation. It was shortly after the installation of the new ESP, that cattle started dying of chronic copper poisoning in the area surrounding the mining complex.

The objective of this study therefore was to examine and describe the distribution and origin of environmental copper in the Phalaborwa region (geobotanical and environmental investigation). Subsequent

field studies in impala and buffalo were conducted to determine the accumulation of copper in the tissues of these animals exposed to high environmental copper concentrations and will be reported separately.

MATERIALS AND METHODS

Geobotanical and environmental description

The geological aspects of the Phalaborwa region are known as the Phalaborwa Igneous Complex (Frick 1986). The region is unique because nowhere else is copper known to occur in economic quantities in association with carbonites (Kuschke & Tonking 1971; Frick 1986). The area that was studied in the KNP, roughly 400 km^2, is between 360 and 410 m above sea level, with a rather flat and monotonous topography. A thick blanket of granitic detritus and scree, which is mostly sandy in composition and varies in thickness, covers the entire area around the town of Phalaborwa. The soil varies from shallow, stony lithosoils along the Olifants River, to more sandy, low clay-content soil in the centre of the complex. The vegetation of the greater part of the Phalaborwa region within the KNP is dominated by open savanna with sparse shrub and a relatively dense grass cover, with *Colophospermum mopane* (mopane) and *Combretum apiculatum* (red bush-willow) being the main tree species (Gertenbach 1983). The region forms part of the Lowveld system with its characteristic semi-arid, warm climate. The long term mean annual rainfall is 481 mm, with a summer rainfall dominance. High temperatures are registered during the summer months, and temperatures of above 40 °C are not uncommon. Mean monthly temperature ranges from 26 °C in January to 16 °C in July and the area is frost-free during winter (Fraser, Van Rooyen & Verster 1987).

Selection of study area

The Phalaborwa region in the KNP that was studied was divided into three zones on the basis of differences in tissue copper concentrations of the initial impala survey in 1989 (Gummow *et al.* 1991) as well as according to variations in the known topsoil copper concentrations for the region. A grid system was superimposed on a 1:50 000 map and the three zones were designated as high-risk (H-r), moderate-risk (M-r) and low-risk (L-r) in relation to the potential for inducing chronic copper poisoning in animals (Fig. 2).

Twelve monitoring sites were selected within the H-r and M-r zones, varying between 1,5 and 9 km from the mining complex (Fig. 2), on the basis of their accessibility from existing roads or firebreaks. Four sites were chosen 60 km north of Phalaborwa to represent the L-r zone and also served as control sites for the investigation (Fig. 1). An additional 11 monitoring sites, on a northeastern transect ranging from 1,6 km from the mining complex to 26 km within the KNP and eight sites outside the KNP, on a northwestern transect (1,2–24 km from the mining complex), were selected (Fig. 2). The sites were identified using small numbered steel plates and steel pins placed on large trees at the different sites.

Geobotanical sampling procedures

All sites were monitored approximately every 4 months, for a period of 2 years, and every 6 months thereafter for an additional 2 years. The monitoring process consisted of collecting from each site three samples of topsoil (<20 mm from the surface and weighing approximately 250 g each), which were mixed together and the composite sample submitted for analysis. In addition, similar composite subsoil samples were collected at a depth of 150 mm from the same sites. All samples were collected within 10 m of the site's marker and placed in strong clear plastic bags that were identified and sealed. At all sampling sites approximately 500 g each of mopane tree leaves and grass plants were collected. The tree leaves were taken from at least five or more mopane trees from the side of the tree facing the mining complex. As far as possible specimens from the same grass species were collected at each monitoring and site, although this was difficult to achieve during winter. *Eragrostis rigidior* was collected at sites 1, 5, 10 and 11; *Cenchrus ciliaris* at sites 3, 6 and 8; *Bothriochloa radicans* at sites 7 and 9, and *Aristida congesta* at sites 2, 4 and 12 (Fig. 2). The grass plants were collected with their roots intact and any adherent soil was removed as far as possible. The leaf and grass samples were placed separately in strong clear plastic bags that were identified and sealed.

Random samples of topsoil, aerial parts of grasses, leaves of trees and forbs were collected from within the H-r zone and the mining complex area during June 1991 to identify the presence of copper accumulator or cuprophilic plants. The plant samples included most of the palatable grass species and the leaves of dominant tree species and forbs.

Sampling from water sources

Water samples were collected monthly from the Olifants River (Fig. 2) and annually from all permanent water sources in the study area (five man-made points and two dams). Whenever available samples were also taken from a small stream and pools formed by seepage from the town's municipal area and golf course. Water samples were collected by the method as described by Hutchinson (1979).

Atmospheric copper sampling

Two monitoring procedures were used to detect either the presence of airborne copper or its fall out.

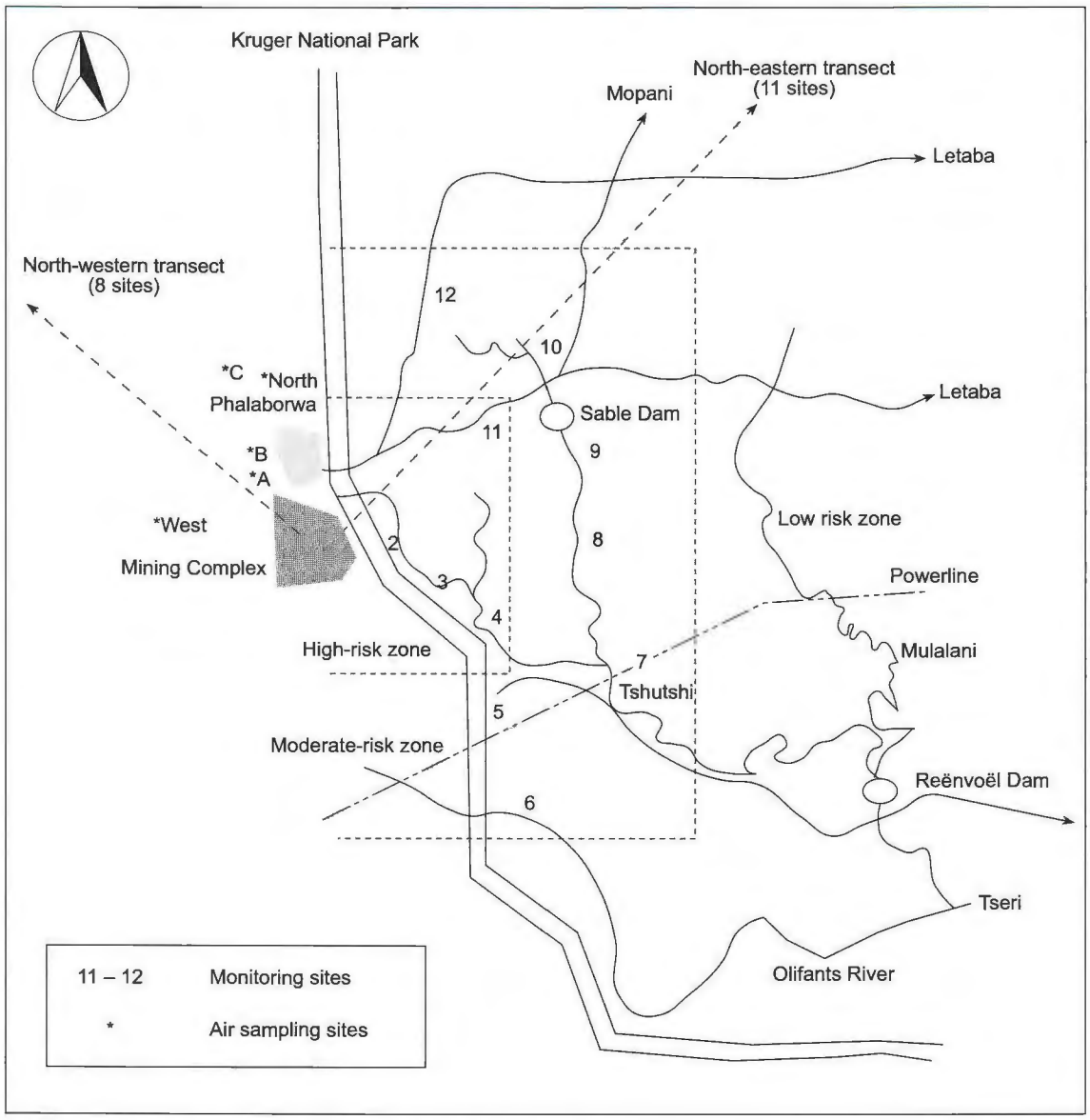

FIG. 2 Risks zones, monitoring sites and transects in the study area

The first method comprised the use of dust fall buckets where four dust fall buckets were used during the period April to August 1991. Two buckets were placed in the KNP at sites 2 and 4; one was placed on the northern side (North) and another on the western (West) side of the mining complex in the municipal area of Phalaborwa (Fig. 2). The buckets in the KNP were positioned 2 m above the ground, on top of wooden poles and those in the municipal area on the roofs of houses. The buckets were conically shaped, 340 mm deep with a mouth diameter of 300 mm. A filter paper disc (grade 1, Whatman), 220 mm in diameter, moistened with liquid paraffin to trap dust particles, was placed at the base of each bucket. A chemically inert plastic mesh with apertures 2 mm in extent was placed over the mouth of each bucket to prevent insects from entering. The filter paper discs were changed every 4 weeks during the monitoring period.

The second method comprised the use of low-volume air sampling monitors (Gil-Air; flow rate 2ℓ/min). Five monitors were used during April 1991 for an average period of 14,4 h in two sessions on alternate days. These monitors were positioned at five different sites, i.e. KNP site 2, three sites in the Phalaborwa town area (A, B and C), and one site on the western side of town (West) (Fig. 2). The sites in relation to the mining complex were either upwind or downwind to the prevailing southeasterly wind. Polycarbonate nucleopore filters (37 mm in diameter, porosity of

0,8 µm) were used in the monitor to collect particulate matter.

Daily wind directions and other climatological parameters, such as rainfall, were obtained from the local weather station in Phalaborwa.

Analyses of samples

Soil and vegetation samples

Soil pH was routinely determined on all soil samples using a similar method as described by Fraser *et al.* (1987). Soil samples were prepared for analysis as described by Parada *et al.* (1987). Roots were carefully pruned from the aerial parts of grass samples and the roots were discarded. Each vegetation sample (aerial part of grasses and leaves) was divided into two aliquots. One aliquot was processed further as collected (unwashed) while the second aliquot was washed by agitation according to the method described by Parada *et al.* (1987). The soil and vegetation samples were then processed and analyzed for mineral content using atomic absorption spectrophotometry according to the method described by Perkin-Elmer Corporation, Norwalk, Connecticut, USA.

Water samples

Copper concentration in water was determined by atomic absorption spectrophotometry.

Dust fall bucket and atmospheric copper

The preparation and analyses of the polycarbonate filters ($n = 10$) from the low-volume air sampling monitors were performed by the Schönland Research Centre, University of the Witwatersrand, Johannesburg using atomic absorption spectrophotometry. Mineral analyses included those for copper, aluminium, zinc, iron and sulphur. Blank samples ($n = 2$) were included for error assessment during calibration and volume measurements.

Dust fall bucket filters were processed and analyzed for copper, aluminium, zinc, iron and sulphur content with the use of atomic absorption spectrophotometry.

Statistical analysis

Various statistical approaches were used to determine the variance of mineral content within an allotted zone, including: testing for differences in mean mineral content, between samples collected from different zones, between topsoil and subsoil, and between washed and unwashed vegetation; and to evaluate the influence of distance from the mining complex and time of year in which the samples were collected on mineral content. All statistical calculations were performed using the Statgraphics 4.0 program (STSC, Statistical Graphics Corporation, Maryland, USA 1989). One-way analysis of variance was used to test for differences in mineral content of soil, water and vegetation between different zones. Scheffé's multiple separation test (Browne 1985) was used to distinguish individual statistical differences in the case of multiple comparisons. A two-way analysis of variance (ANOVA) of the mean mineral analysis data of topsoil and subsoil; washed and unwashed grass; and washed and unwashed leaves, with distance from the mining complex and time of the year as the main effects, was performed. Linear regression was done on topsoil samples of the northeastern transect within the KNP and on topsoil samples of the northwestern transect outside the KNP, according to a multiplicative model (Statgraphics 4.0).

RESULTS

Soil and vegetation samples

Comparisons of the mean copper concentrations of soil, grass and leaves collected at intervals over a period of 3 years within the H-r and M-r zones and the control area are summarized in Table 1 and the means of copper concentrations over the entire study period in Table 2.

Significant differences ($P \leq 0,05$) were observed between the mean topsoil copper concentrations of the H-r zone (168,1 ± 91,5 ppm DM), M-r zone (54,2 ± 20,9 ppm DM) and control area (17,1 ± 6,4 ppm DM). No significant differences existed between the mean subsoil copper concentration of the H-r zone (41,0 ± 14,2 ppm DM) and the M-r zone (30,9 ± 13,2 ppm DM). The difference between the mean subsoil copper concentration from the H-r zone and control area (16,6 ± 5,2 ppm DM) was significant ($P \leq 0,05$). Significant differences existed between the means of the copper concentrations of unwashed leaves and grass from the H-r zone when compared to the control area ($P \leq 0,05$).

Soil pH within the H-r zone measured between 6,7 and 7,0 and between 7,1 and 7,4 within the M-r zone. The soil pH measured between 7,0 and 7,3 in the control area.

Data presented in Table 3 depict copper concentrations in grasses and leaves of trees and forbs (all washed before copper determination) selectively sampled in an attempt to identify copper accumulator species. No true copper accumulators were identified within the KNP, but very high copper concentrations were determined in certain grasses growing within the industrial property of the mining complex.

There was a significant difference ($P \leq 0,05$) between the combined mean unwashed grass copper concentration of the H-r zone (58,9 ± 36,7 ppm DM) and the control area (14,1 ± 4,9 ppm DM). The difference between the mean unwashed grass copper concentration (58,9 ± 36,7 ppm DM) and the mean washed

TABLE 1 Comparison of mean (± SD) copper concentrations (ppm DM) of soil, grass and mopane leaves at various intervals throughout the trial period within the High-risk and Moderate-risk zones of the Phalaborwa complex and the control area within the KNP

Time of collection	Mean copper concentrations ± SD (ppm DM)		
	High-risk zone		
	Soil[a]	Grass[b]	Leaves[c]
Feb. 1990	148,6 ± 63,4 : 40,4 ± 11,3	51,8 ± 17,8 : 32,4 ± 8,5	43,6 ± 7,9 : 31,0 ± 7,7
Jun. 1990	191,8 ± 108,4 : 39,2 ± 10,1	82,8 ± 20,8 : 54,8 ± 11,9	108,4 ± 25,5 : 79,4 ± 20,7
Nov. 1990	146,9 ± 70,9 : 40,4 ± 11,4	72,6 ± 26,0 : 39,6 ± 10,4	22,6 ± 9,1 : 19,0 ± 5,3
Feb. 1991	163,2 ± 101,9 : 34,2 ± 8,8	26,4 ± 6,9 : 19,4 ± 4,0	20,8 ± 9,9 : 16,6 ± 6,4
Jun. 1991	151,8 ± 81,4 : 33,2 ± 8,9	36,2 ± 8,1 : 26,2 ± 8,1	41,8 ± 14,8 : 27,4 ± 10,7
Nov. 1991	139,6 ± 71,0 : 35,8 ± 8,3	50,8 ± 24,2 : 43,2 ± 22,9	60,6 ± 33,2 : 41,0 ± 16,0
Feb. 1992	243,2 ± 174,8 : 39,8 ± 6,4	57,8 ± 61,1 : 27,4 ± 9,1	13,6 ± 4,2 : 14,2 ± 3,5
Jul. 1992	165,2 ± 60,8 : 64,2 ± 22,4	98,0 ± 57,2 : 66,4 ± 43,5	43,4 ± 19,5 : 33,8 ± 11,8
Feb. 1993	162,8 ± 68,8 : 42,2 ± 15,5	54,4 ± 26,4 : 41,4 ± 18,2	11,8 ± 1,8 : 11,0 ± 1,0
	Moderate-risk zone		
Feb. 1990	63,7 ± 15,0 : 36,4 ± 16,2	29,6 ± 7,5 : 23,1 ± 5,2	27,7 ± 6,2 : 20,1 ± 1,9
Jun. 1990	57,7 ± 18,0 : 38, ± 18,4	54,9 ± 13,1 : 37,6 ± 10,3	64,4 ± 34,8 : 36,1 ± 6,4
Nov. 1990	40,3 ± 14,7 : 31,1 ± 12,5	43,1 ± 14,6 : 26,0 ± 9,8	18,1 ± 4,4 : 17,0 ± 3,9
Feb. 1991	69,1 ± 29,7 : 32,0 ± 13,4	12,6 ± 1,2 : 9,4 ± 1,8	12,6 ± 1,1 : 12,9 ± 3,2
Jun. 1991	41,3 ± 15,8 : 24,0 ± 11,3	22,6 ± 5,2 : 16,0 ± 3,9	24,1 ± 4,1 : 15,6 ± 5,1
Nov. 1991	40,7 ± 11,7 : 28,0 ± 15,5	21,7 ± 10,4 : 19,3 ± 7,4	28,9 ± 16,0 : 23,3 ± 12,8
Feb. 1992	54,4 ± 16,5 : 26,6 ± 9,6	27,4 ± 13,3 : 15,4 ± 4,8	14,4 ± 7,8 : 12,7 ± 5,6
Jul. 1992	59,6 ± 17,8 : 31,9 ± 11,4	48,1 ± 31,8 : 36,7 ± 19,2	27,3 ± 8,0 : 18,9 ± 3,3
Feb. 1993	61,1 ± 27,5 : 30,0 ± 9,9	26,0 ± 12,4 : 22,0 ± 7,8	15,0 ± 4,2 : 12,9 ± 1,8
	Control area		
Feb. 1990	17,0 ± 5,0 : 16,8 ± 5,1	14,8 ± 2,6 : 14,5 ± 1,9	14,0 ± 2,8 : 14,8 ± 2,5
Jun. 1990	17,8 ± 10,1 : 14,0 ± 6,0	20,5 ± 8,3 : 20,8 ± 7,3	13,8 ± 3,4 : 14,0 ± 3,2
Nov. 1990	16,0 ± 4,1 : 16,3 ± 4,6	16,8 ± 5,1 : 16,8 ± 4,5	7,5 ± 0,6 : 9,5 ± 1,3
Feb. 1991	12,8 ± 7,8 : 15,3 ± 10,9	9,5 ± 3,6 : 10,8 ± 3,0	8,8 ± 1,7 : 9,8 ± 2,8
Jun. 1991	20,8 ± 8,4 : 17,8 ± 2,2	14,3 ± 3,3 : 14,3 ± 1,7	10,3 ± 2,4 : 12,5 ± 2,6
Nov. 1991	15,5 ± 5,9 : 16,5 ± 5,4	11,8 ± 0,9 : 13,3 ± 2,2	12,0 ± 1,4 : 13,0 ± 2,7
Feb. 1992	20,5 ± 7,1 : 18,0 ± 5,3	12,8 ± 5,7 : 13,5 ± 3,8	8,8 ± 0,5 : 9,0 ± 0,8
Jul. 1992	18,8 ± 4,3 : 20,0 ± 2,0	14,3 ± 1,7 : 13,8 ± 1,3	15,5 ± 2,5 : 15,0 ± 2,4
Feb. 1993	15,0 ± 3,1 : 15,0 ± 3,6	12,8 ± 3,9 : 12,8 ± 3,9	9,8 ± 2,2 : 9,5 ± 1,9

[a] Topsoil: subsoil
[b and c] Washed: unwashed

TABLE 2 Comparison of mean (± SD) copper concentrations (ppm DM) of geobotanical samples collected within the High-risk zone and Moderate-risk zone of the Phalaborwa complex and control area within the KNP over the entire study period

Sample		Mean copper concentration ± SD (ppm DM)		
		High-risk (n = 45)	Moderate-risk (n = 63)	Control area (n = 36)
Soil:	Topsoil	68,1 ± 91,5[a]	54,2 ± 20,9[b]	17,1 ± 6,4[c]
	Subsoil	41,0 ± 14,2[b]	30,9 ± 13,2[b, c]	16,6 ± 5,2[c]
Grass:	Unwashed	58,9 ± 36,7[a]	31,8 ± 18,9[b]	14,1 ± 4,9[b]
	Washed	38,9 ± 22,2[a]	22,8 ± 12,4[b]	14,5 ± 4,3[b]
Leaves:	Unwashed	40,7 ± 32,6[a]	25,8 ± 19,7[b]	11,1 ± 3,3[b]
	Washed	30,4 ± 22,3[a]	18,8 ± 8,9[b]	11,9 ± 3,1[b]

[a, b, c] Values for soil, grass and leaves with different superscripts are significantly different ($P \leq 0,05$)

TABLE 3 Copper concentrations (ppm DM) of washed leaves of trees, forbs and grasses within the High-risk zone of the KNP and within the Phalaborwa mining area (MA)

Plants	Mean (range) copper concentrations (ppm DM)	
	Topsoil	Plants
Forb species		
Heliotropium steudneri	232	37 (33–47)
Crotalaria virgulata	232	26 (20–41)
Solanum panduriforme	214	29 (n = 1)
Ceratotheca triloba	214	42 (27–51)
Grass species		
Cenchrus ciliaris	7232 (MA)	811 (632–1476)
	248	77 (68–114)
Themeda triandra	146	39 (n = 1)
Enneapogon cenchroides	7232 (MA)	323 (129–439)
Panicum maximum	248	82 (65–93)
Urochloa mosambicensis	109–184	48 (45–52)
Eragrostis rigidior	232–314	61 (43–81)
Tree species		
Combretum apiculatum	232–314	58 (40–83)
Cassia abbreviata	109	40 (33–47)
Lonchocarpus capassa	184	29 (n = 1)
Terminalia sericea	232	67 (n = 1)

TABLE 4 ANOVA table for mean top- and subsoil copper concentrations and distance away from the smelter over the entire study period

Source of variation	Sum of squares	Degrees of freedom	Mean square	F-ratio	Significance
Main effects					
A = Distance	38 350,52	2	19 175,26	32,05	0,001
B = Top- or subsoil Cu	19 178,45	1	19 178,45	32,05	0,001
Interactions: AB	22 243,84	2	11 121,92	18,59	0,001
Residual	15 558,08	26	598,39		

TABLE 5 Mean (± SD) of copper, zinc, molybdenum and iron concentrations (ppm DM) for top- and subsoil at various sites within the study area

Site	Mean (± SD) mineral concentration (ppm DM)			
	Copper	Zinc	Molybdenum	Iron
Mining area				
Topsoil	1628 ± 1324[a]	84 ± 51	31 ± 16	4760 ± 3983[a]
Subsoil	532 ± 498	40 ± 34	33 ± 13	1750 ± 1456
High-risk				
Topsoil	202 ± 143[b]	47 ± 41	29 ± 11	1240 ± 1342[b]
Subsoil	55 ± 43	31 ± 18	37 ± 17	940 ± 768
Moderate-risk				
Topsoil	88 ± 36	32 ± 16	38 ± 15	770 ± 453
Subsoil	39 ± 16	30 ± 14	37 ± 11	840 ± 521
Control				
Topsoil	22 ± 10[c]	24 ± 7	32 ± 10	670 ± 234[c]
Subsoil	18 ± 7	28 ± 9	30 ± 8	700 ± 307

Note: Most figures were rounded off
[a, b, c] Values for different superscripts are significantly different ($P \leq 0,05$)

grass copper concentration (38,9 ± 22,2 ppm DM) within the H-r zone was also significant ($P \leq 0,05$). The H-r zone's washed grass copper concentration was significantly higher ($P \leq 0,05$) than control washed grass copper concentration. No significant difference ($P > 0,05$) existed between mean copper concentration of washed and unwashed grass in the M-r zone, although the unwashed copper concentration was consistently higher than the washed copper concentration of the same grass samples.

A similar significant difference ($P \leq 0,05$) between the combined mean unwashed tree leaf copper concentration of the H-r zone (40,7 ± 32,6 ppm DM) and the control area (11,1 ± 3,3 ppm DM) was observed. However, the difference between the mean unwashed leaf copper concentration of the H-r zone (40,7 ± 32,6 ppm DM) and the mean washed leaf copper concentration (30,4 ± 22,3 ppm DM) was not significant although the unwashed leaf samples generally had a higher copper concentration than washed leaf samples. Within the control area no significant difference existed between the copper concentrations of washed and unwashed grass, or washed and unwashed leaves.

The ANOVA results of the effect of soil depth (i.e. topsoil and subsoil) and distance from the smelter on mean copper concentrations, over the entire study period, are given in Table 4.

The main effects of soil depth and distance from the smelter, using date as a blocking factor, were found to be highly significant ($P < 0,01$). The interaction between distance and soil copper concentration on the surface and at depth was also highly significant ($P < 0,01$), indicating an increase in topsoil relative to subsoil copper concentration the shorter the distance from the smelter (i.e. within the H-r zone).

It was possible to predict topsoil copper concentrations along the northeastern transect into the KNP and the northwestern transect outside the KNP extremely well, using a linear regression multiplicative model (Fig. 3). Between 90 and 97% of the possible topsoil copper concentrations along the northwestern transect could be explained by distance from the smelter. A slightly lower, but still highly significant prediction between 72 and 86% could be explained by the same model on the northeastern transect. The dotted line closest to the graph's curve, represents the decline in copper concentrations within the 95% confidence limit, whilst the other dotted line represents expected future predictions within the 95% confidence limit.

Due to the various interactions of copper with other elements, analyses were done to test for zinc, iron and molybdenum concentrations in all the soil samples. Zinc, iron and molybdenum are known to alter the availability of copper in the normal metabolism

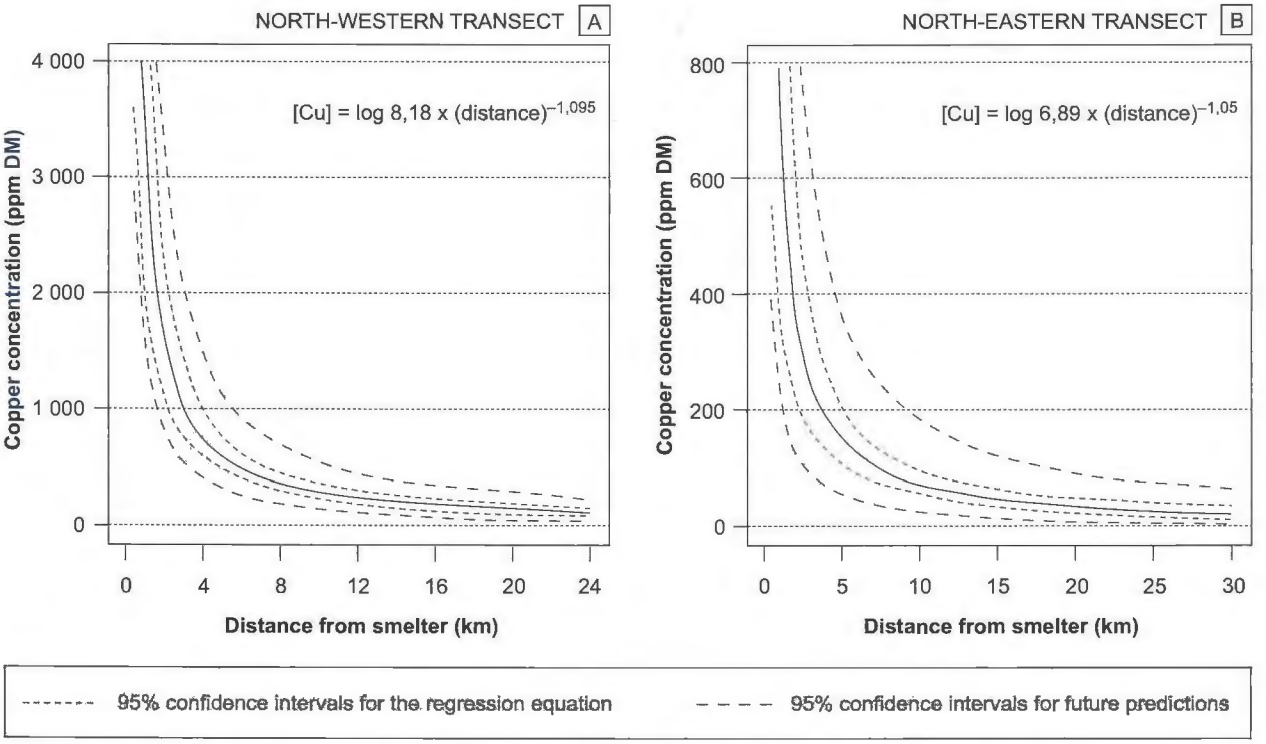

FIG. 3 Regression of topsoil copper concentration (ppm DM) on distance away from the copper smelter along the north-eastern and north-western transects

TABLE 6 Copper concentrations (ppm DM) of filter paper collected from dustfall buckets

Period of collection	Copper concentration (ppm DM)			
	Site 2	Site 4	North*	West*
February 1990	21	11	69	24
March 1990	17	9	101	41
April 1990	18	18	44	20
May 1990	84	28	53	11
Mean ± SD	35,0 ± 32,7[a]	16,5 ± 8,6[a]	66,8 ± 25,1[b]	24,0 ± 12,6[a]

[a, b] Means with different superscripts are significantly different ($P \leq 0,05$)
* Position relative to mining complex

TABLE 7 Mineral concentrations (g/m^3) recorded using low-volume air sampling monitors during April 1991

Site		Mineral concentrations (µg/m^3)				
		Wind	Copper	Zinc	Aluminium	Sulphur
KNP site 2	Day 1	SE	0,025	0,023	1,559	1,021
	Day 2	None	0,041	0,035	1,538	1,212
Town A	Day 1	SE	0,170	0,365	0,872	1,702
	Day 2	SSE	0,120	0,045	0,691	1,125
Town B	Day 1	SE	0,172	0,041	1,224	1,230
	Day 2	SE	0,187	0,051	0,830	1,408
Town C	Day 1	SE	0,268	0,394	0,848	1,289
	Day 2	SE	0,231	0,063	1,377	2,143
West	Day 1	SE	0,093	0,046	1,102	1,634
	Day 2	SSE	0,075	0,063	1,135	1,406

of copper in animals (Suttle 1981). Mean values were calculated for the three elements within the three different zones and are presented in Table 5.

Molybdenum concentration was generally high in all soil samples, with no significant differences ($P > 0,05$) between surface soils and deep soils in any of the zones. This remained constant at all sites throughout the study period, whereas zinc and iron concentrations varied. Topsoil iron concentration recorded within the H-r zone was significantly higher ($P \leq 0,05$) than topsoil iron concentration of control soil samples.

Water samples

Copper concentrations in water were found to be low and within the normal limits (50–200 µg/ℓ) as accepted for both human and animal drinking water standards (Piscator 1979).

Atmospheric copper

The copper concentrations determined on the filter paper discs placed in dust fall buckets are presented in Table 6 and the concentrations of various minerals on the filters of the low-volume air sampling monitors in Table 7 (refer to Fig. 2).

Results of dust fall bucket data confirmed the presence of copper fall out within the study area. Copper concentrations measured north of the mining complex were significantly higher ($P \leq 0,05$) than copper concentrations measured within the KNP during the first 4 months of the investigation. Low-volume air sampling monitors were used to confirm the presence of airborne copper in the Phalaborwa region. Although the copper concentrations measured by this method were considerably lower than those measured using the dust fall bucket method, considerable copper concentrations were measured. Copper concentrations measured upwind in the KNP were lower than those measured downwind from the smelter at site C in Phalaborwa.

Rainfall figures for the entire study period indicated two very dry periods: the 19 months of very low rainfall during 1988 and 1989, and the 21 months of continuous low rainfall measured in 1991 and 1992, resulted in severe drought conditions.

The predominant wind direction during the years under investigation was from the southeast (45–60%) while the three other main directions were from the southwest (7–11%), south (10–20%) and north (8–15%).

DISCUSSION

The levels of topsoil copper concentration measured indicate that copper contamination had occurred in

the immediate vicinity of the smelter, and to the east, northeast and southeast of it in the study area within the KNP. This is evident as topsoil within the H-r zone had statistically higher ($P \leq 0,05$) concentrations of copper than those sampled at a depth of 15 cm, as well as by the significant decline in topsoil copper concentration with increasing distance from the smelter, particularly on the side of the prevailing winds. Topsoil copper concentration of samples from the H-r zone were also significantly higher than samples from the control area ($P \leq 0,05$). No statistical difference ($P > 0,05$) existed between top- and subsoil cop-per concentrations sampled within the control area.

Unwashed plant analyses within the study area consistently yielded higher copper concentrations than the washed plant samples from the same site. Using one-way analysis of variance, together with Scheffé's multiple separation test, copper concentrations of unwashed grass samples within the H-r zone were significantly higher than those of corresponding washed samples ($P \leq 0,05$). The lower copper concentrations in washed grass and leaf samples, suggest that copper was contained as dust on the plants' surface, supporting the hypothesis of the presence of airborne copper within the study area. The difference between washed plant samples within the M-r zone and the control area was not significant ($P \geq 0,05$).

Much is known and has been reported on the accumulation of copper and other heavy metals in soils in the vicinity of smelters. Heavy metals selectively accumulate in the organic layers of soils, binding tightly and replacing less tightly bound ions such as Ca^{2+}, Mg^{2+} and K^{+} (Hutchinson 1979). The availability, stability and fate of copper in this form depend on various physico-chemical factors, e.g. soil pH and chemical form.

Soil pH affects solubility and mobilization of copper in the soil and it's availability to plants. Increased solubility and mobilization are observed in more acidic soil types. Hutchinson (1979) reported that mobilization only occurs at a pH < 3. The soil pH determined was considerably higher than the pH level under which appreciable mobilization of copper would take place. It is therefore unlikely that the accumulation of copper in the topsoil could have resulted from mobilization from deeper soil layers.

The chemical form of copper affects its solubility. Copper in the form of sulphate and sulphide is water soluble and can therefore be readily mobilized, whereas the oxide is insoluble (Hutchinson 1979). Analyses within the study area confirmed that the majority of copper forms were either sulphates, sulphides or oxides. Similar results were obtained from the smelter emissions. In-stack tests showed that the emissions contained 35,7 % total copper of which 10,6–20,7 % was available as copper sulphate or cupric sulphide, resulting from interaction with sulphur oxides emitted during the smelting process (Van Rensburg, personal communication 1994, Main Chemical Laboratory, PMC). The insoluble copper was present as cupric or cuprous oxides (Van Rensburg, personal communication 1994, Main Chemical Laboratory, PMC).

These emissions could therefore account for the accumulation of copper in the topsoil within the H-r zone in relation to the other zones. The presence of the soluble forms would also explain the mobilization of copper into the subsoil. The importance of copper accumulated in soil is determined by the total amount available for uptake by plants and animals. Only extractable or water-soluble copper is available for uptake by plants (Hutchinson 1979), whereas animals are able to utilize copper from plant uptake as well as insoluble forms deposited on vegetation. Insoluble copper oxide forms are used therapeutically to supplement copper in domestic animals deficient in the mineral (Suttle 1981). Available copper concentrations above the critical level of 20 ppm DM were only obtained within the mining complex and the H-r zone (Van Rensburg, personal communication 1994, Main Chemical Laboratory, PMC).

The availability of soil copper for uptake by plants is determined by various factors. Soil pH, the specific plant species involved, the copper concentration of the soil and the growth season, are some factors determining the copper status of a plant. A general observation was that higher copper concentrations were found in plants in the higher copper concentration soils. Grasses had constantly higher copper concentrations than tree foliage at the same copper soil concentration, as determined from the copper analyses of washed plant material. These observations are supported by results reported by Hutchinson (1979). The grasses, *Cenchrus ciliaris* and *Enneapogon cenchroides*, both being palatable species for wild herbivores (Gertenbach 1983), contained the highest copper concentrations. Wild (1968) also measured high copper concentrations in these species on copper rich soils in Zimbabwe, but also reported the presence of various accumulator species or cuprophiles, none of which could be found within the study area. However, various forbs and other grasses sampled within the H-r zone and around the mining complex, had moderate to high copper concentrations. *Cenchrus ciliaris* copper concentrations were very high on the smelting site. Copper concentrations of grasses within the H-r zone were much lower, but were still significantly higher than those of the M-r zone and control area grass samples collected during the same period.

Large particulate matter, which becomes suspended in the atmosphere by wind forces or mechanical means, and other particulate matter cleansed from the atmosphere by rain or agglomeration, can be

measured by using an open mouth container exposed for a period of approximately one month (Gummow *et al.* 1991). Results of dust fall bucket data confirmed the presence of copper fall out in the Phalaborwa region. Significantly higher ($P \leq 0,05$) copper concentrations than those measured in the KNP were measured north of the mining complex. This finding could be partly explained by the prevailing winds during the collection period, which blew predominantly from the south and southeast. During May 1990 the direction changed, with a greater percentage of wind blowing from the west and northwest, increasing the possibility of particulate dust fall from the mining complex to the adjacent KNP. As a consequence a copper concentration of 84 ppm DM was measured at site 2 in the KNP, significantly higher ($P < 0,05$) than those measured in Phalaborwa (Table 6).

Low-volume air sampling monitors were used to confirm the presence of airborne copper in the Phalaborwa region. Although copper concentrations measured were low, higher concentrations were measured downwind than upwind from the mining complex, indicating the major role wind plays in the area in dispersing particulate matter. Winds from the south to southeast and east (80 %) predominated during the summer months, while north to northwesterly wind directions increased during the winter months, with south to southeasterly winds (50 %) still predominating, although to a lesser degree. Particulate matter from the mining complex would therefore be transported mainly away from the KNP by these southeasterly winds, whereas the westerly and northwesterly winds would transport these particulates directly into the KNP. The proximity of the smelter stack to the border of the KNP increased the possibility of direct fallout of particulates into the H-r zone during wind-still days. Although copper concentrations measured by this method were considerably lower than the dust fall bucket method, copper concentrations measured upwind in the KNP were lower than those measured downwind from the smelter in Phalaborwa's municipal area.

It was further possible to empirically calculate the dust fall rate in terms of grams per square meter per month as follows, using a method described by Herrick (1966):

$$\text{Dustfall} = (W/a)x(30/t)$$

where dust fall = g/m² per month
W = mass analyzed in grams
a = open area of sampling container (0,38 m²)
t = time of exposure days (28 d)

Applying this formula, dustfall of 1 g/m² will equal 1,78 ton/km² (2,86 ton/square mile).

The rate of environmental copper pollution as a result of the mining operations was determined according to the amounts of copper mined per day as well as predictions from Herrick's (1966) formula. According to this formula, and using the mean monthly concentration of copper collected in the dustfall buckets over a period of 4 months, a monthly rate of pollution of 0,987 g/m² or 1759 kg/km² at site 2 in the KNP and 0,465 g/m² or 827 kg/km² for site 4 could be predicted.

Little or no copper contamination of the water sources occurred within the study area. The copper concentrations measured were slightly, but not significantly, higher than acceptable water copper concentrations. It was therefore unlikely that the water served as a source of contamination of animals in the KNP.

Rainfall and drought periods had a major influence on the accumulation of copper within the study area. The highest copper concentrations within the H-r zone were measured in plants during the dry seasons. During the same period the difference between washed and unwashed copper analyses were also significantly greater than during the wet periods ($P < 0,05$ (Table 1).

The elevated copper concentrations measured in the various plant tissues within the study area were as high or higher than copper concentrations measured during documented cases of chronic copper poisoning outbreaks in domestic animals (Bath 1979; Parada *et al.* 1987). As the potential existed to affect wildlife in the KNP according to geobotanical findings, the influence of these high copper concentrations on certain species of wildlife was further investigated.

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