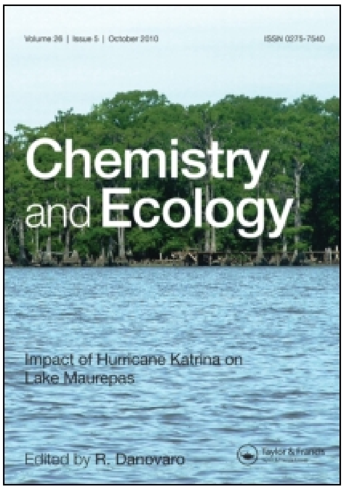

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

Heavy metals contents of roadside mosses in the northern and south-eastern regions of Nigeria

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Online publication date: 14 September 2010

To cite this Article Onianwa, P. C. and Ajayi, S. O.(2002) 'Heavy metals contents of roadside mosses in the northern and south-eastern regions of Nigeria', Chemistry and Ecology, 18: 3, 187 — 194
To link to this Article: DOI: 10.1080/02757540215053
URL: http://dx.doi.org/10.1080/02757540215053

Chemistry and Ecology, 2002, Vol. 18(3–4), pp. 187–194

HEAVY METALS CONTENTS OF ROADSIDE MOSSES IN THE NORTHERN AND SOUTH-EASTERN REGIONS OF NIGERIA

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(Received 14 March 2001; Accepted 15 May 2001)

Levels of lead, zinc, cadmium, copper and nickel were determined in roadside moss samples within towns in the northern and south-eastern regions of Nigeria. Average lead level in the south-east (59 ppm) was higher than the average for the northern region (44 ppm). Average levels of zinc, cadmium, copper and nickel did not differ significantly between the two regions, with overall averages for the entire study area being 50.9, 1.2, 11.3 and 5.6 ppm for these metals. Lead levels were poorly correlated with those of the other metals, indicating that automobile emissions may not be the main source for these metals in the moss. In comparison with a previous study of the south-west region, the results indicate a generally slightly higher level of metal pollution in the south-west region than in both the northern and south-eastern regions.

Keywords: Moss; Heavy metals; Lead, Nigeria

INTRODUCTION

Heavy metal contamination of the environment may be derived from the use of products of the chemical industry such as fossil fuels. Because of the hazardous nature of some heavy metals to human health, the monitoring of the environmental burden of heavy metals is an important ecological interest. Epiphytic mosses have been found particularly useful for monitoring atmospheric heavy metal burden (Onianwa, 2001) because of their unique morphology and ecology. They have no true roots or vascular systems and are able take up nutrients from the atmosphere by particulate trapping and sorption. This usually involves ion exchange and chelation (Ruhling and Tyler, 1970; Andre and Pijarowski, 1977; Manning and Feder, 1980; Richardson, 1981; Onianwa, 1986b; Crist *et al.*, 1996).

Mosses have been used to map the deposition patterns of airborne metals over large areas. Such regional surveys have been carried out in Sweden (Ruhling and Tyler, 1968, 1969, 1971, 1973; Ruhling and Skarby, 1979; National Swedish Environmental Protection Board, 1983), Finland (Pakarinen and Tolonen, 1976; Pakarinen, 1978), USA (Groet, 1976), Denmark (Pilegaard *et al.*, 1979), Poland (Grodzinska, 1978; Grodzinska *et al.*, 1993), Greece (Sawidis, 1993), Norway (Steinnes, 1977; Hvatum *et al.*, 1983), and

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ISSN 0275-7540 print; ISSN 1029-0370 online
DOI: 10.1080/0275754021000065862

Nigeria (Onianwa *et al.*, 1986a; Onianwa and Ajayi, 1987), among others. Some of these surveys involved the monitoring of metal levels in mosses found in the areas of motorways.

In the survey of the south-western region of Nigeria (Onianwa and Ajayi, 1987), levels of heavy metals were determined in roadside mosses within towns and villages in the region. From the results, zones of varied levels of pollution for lead and other metals were mapped. The south-west region of Nigeria represents less than 20% of the 924 000 km^2 land mass of the country. No similar moss survey is reported in the literature for the vast northern region and the south-eastern region. The aim of this study therefore was to determine the contents of heavy metals in roadside mosses within the said northern and south-eastern regions of Nigeria, with a view to discerning variations in relative pollution levels.

MATERIALS AND METHODS

Moss samples were collected during September–October 1989, and were analysed immediately after collection. They were mostly of acrocarpous and pleurocarpous species, *Barbula lambarenensis, Bryum coronatum, Rhacopilium orthocapoides, Stereophylum virens, Calymperes* sp., and *Thuidium gratum*, growing on walls of buildings and on tree barks. About 30 towns were sampled in the northern region, and 39 in the south-east (Tables I and II; Fig. 1). The ecology of the north is characterised by a drier hotter climate than the

TABLE I Concentrations (ppm) of metals in roadside moss samples from the northern region

	Geographic Location						
Town	*(N)*	*(E)*	*Lead*	*Zinc*	*Cadmium*	*Copper*	*Nickel*
Abuja	9 10	7 08	92.1	76.3	<0.02	12.0	11.2
Alliade	7 16	8 29	1.3	48.8	1.3	4.9	2.9
Auno	11 51	12 57	10.3	11.6	3.3	15.1	<0.05
Azare	11 39	10 11	15.6	42.2	2.0	4.7	2.9
Bama	11 23	13 41	20.0	20.6	3.0	9.3	10.3
Birnin Kudu	11 27	9 30	1.4	48.0	4.6	12.0	5.4
Damaturu	11 57	11 44	12.0	55.9	2.0	16.1	16.5
Girei	9 26	12 32	1.3	21.2	0.17	5.8	5.6
Gombe	10 17	11 10	45.5	14.2	<0.02	79.5	9.6
Gwabada	10 15	7 18	4.0	15.0	0.03	6.5	0.13
Gwarzo	11 55	7 56	25.0	14.6	0.72	5.3	<0.05
Gwoza	11 05	13 43	13.8	12.1	0.25	9.5	<0.05
Kaduna	10 28	7 25	210	29.2	2.5	26.9	6.3
Kari	11 13	10 33	10.3	189	0.61	21.2	<0.05
Koton-Karfi	8 05	6 50	11.6	50.0	0.59	7.0	6.2
Lokoja	7 49	6 44	73.1	29.2	<0.02	8.2	14.5
Maiduguri	11 50	13 51	130	33.5	0.50	6.6	<0.05
Makurdi	7 44	8 38	73.8	11.6	0.25	9.8	7.9
Mubi	10 16	13 14	5.0	51.3	<0.02	9.5	<0.05
Numan	9 27	12 03	10.4	12.1	4.2	12.5	<0.05
Okene	7 36	6 10	28.0	33.4	3.63	13.0	2.6
Oturkpo	9 51	8 08	22.6	20.4	<0.02	7.5	2.0
Potiskum	11 43	11 04	35.0	20.0	1.75	7.5	9.1
Shika	11 09	7 35	1.3	48.1	0.96	4.0	3.6
Talata Mafara	12 33	6 04	15.9	104	0.13	15.4	1.0
Toto	8 22	7 07	2.8	22.9	0.50	6.9	8.4
Wukari	7 52	9 46	107	20.6	3.1	16.1	12.5
Yola	9 14	12 32	327	25.0	<0.02	8.1	10.1
Zaria	11 06	7 44	14.6	45.0	4.1	4.9	6.3
Zoro	11 39	11 20	10.5	18.8	1.0	6.6	5.9

TABLE II Concentrations (ppm) of metals in roadside moss samples from the south-east region

Town	*Geographic Location* (N)	(E)	*Lead*	*Zinc*	*Cadmium*	*Copper*	*Nickel*
Aba	5 06	7 21	162	18.3	0.42	17.8	6.9
Abudu	6 02	6 03	63.8	72.5	<0.02	6.8	6.0
Afikpo	5 53	7 57	33.0	16.4	2.7	9.3	12.3
Agbor	6 12	6 10	207	32.0	0.03	8.8	0.80
Amaigbo	5 27	7 25	13.9	60.0	<0.02	3.6	<0.05
Asaba	6 10	6 45	73.1	13.8	2.1	4.6	7.6
Benin	6 25	5 30	109	100	<0.02	68.8	<0.05
Calabar	4 50	8 15	57.5	41.3	0.50	6.6	4.3
Elele	5 07	6 47	12.5	77.5	1.5	42.5	0.75
Enugu	6 27	7 22	78.3	18.8	<0.02	2.8	5.0
Etiti	5 34	7 26	8.0	95.5	<0.02	5.1	1.5
Ezinachi	5 43	7 25	56.3	20.8	0.75	5.5	13.8
Ibusa	6 10	6 39	30.0	163	0.11	11.8	4.1
Ihiala	5 50	6 53	23.3	108	0.38	8.1	3.6
Ikot-Ekpene	5 10	7 43	23.8	67.5	0.06	7.1	7.8
Isiokpo	5 01	6 53	56.4	13.8	<0.02	6.1	4.9
Issele-Uku	6 19	6 30	8.0	43.8	3.77	12.1	8.9
Itu	5 13	7 59	71.3	154	3.0	8.9	5.0
Mgbidi	5 58	6 54	56.8	17.8	0.82	5.6	1.2
Ngwo	6 03	7 20	19.0	17.5	3.4	13.2	3.4
Obehie	5 02	7 15	18.4	12.5	1.0	6.4	3.4
Obigu	5 01	7 19	13.7	28.0	2.6	5.2	11.0
Obolo	6 57	7 32	10.3	17.5	0.75	3.6	18.1
Ogwashi-Uku	6 09	6 33	34.8	16.3	<0.02	3.5	10.9
Okigwe	5 49	7 21	59.0	17.5	0.25	10.1	1.5
Okija	5 51	6 53	11.4	52.2	4.2	7.6	1.9
Okpala Ngwa	5 21	7 23	15.6	91.3	<0.02	21.9	9.6
Okpanam	6 11	6 40	16.3	319	0.46	6.7	6.8
Onitsha	6 10	6 47	272	17.5	<0.02	9.4	7.0
Opi	6 48	7 26	9.2	37.8	<0.02	7.4	7.5
Owerri	5 29	7 02	84.0	15.0	0.75	8.5	12.9
Ozubulu	5 57	6 53	29.8	41.7	3.5	18.3	6.1
Port-Harcourt	4 43	7 05	232	52.5	1.4	8.3	6.8
Rumuigbo	5 09	7 01	27.5	51.4	1.6	5.1	4.0
Ukehe	6 21	7 26	7.0	16.1	0.81	5.4	2.8
Umu-Nelu	5 10	6 53	10.0	108	0.63	5.8	3.8
Umuahia	5 31	7 26	169	92.5	0.75	8.5	<0.05
Umunede	6 16	6 18	62.5	73.8	0.11	7.5	6.8
Uyo	5 00	7 55	48.1	155	1.0	2.1	6.5

relatively more humid southern region. Moss samples were thus more sparsely distributed in the northern zones. In each town, samples of moss were collected at roadsides along the busiest roads, and carefully handled to avoid contamination.

The samples were picked by hand from wall surfaces or tree trunk and stored in paper envelopes. Because the sampling period was within the rainy season dust contamination was insignificant. Some samples contained entrapped tree bark and similar debris, which were removed by hand-picking or by use of a camel-hair brush. Cleaned samples were ground using a porcelain mortar, dried at $70 - 80°C$ in an oven, cooled in a desiccator, and then weighed portions were wet-digested with a 4:1 mixture of nitric-perchloric acids. The digests were subsequently made up with distilled water, and analysed for the metals lead, zinc, cadmium, copper and nickel by atomic absorption spectrophotometry (Perkin Elmer 2380), using the most sensitive absorption lines. The instrument was operated in

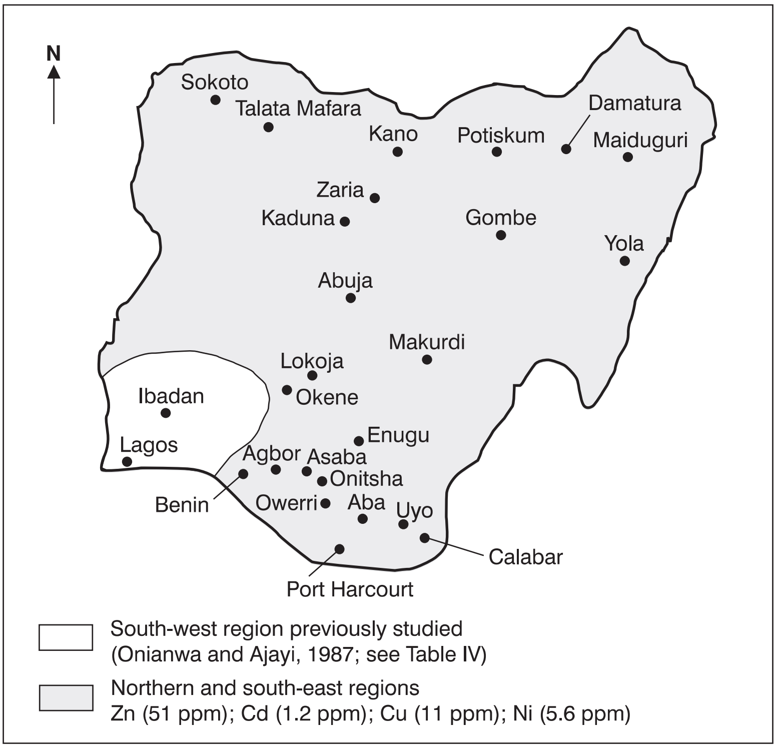

FIGURE 1 Map of Nigeria showing study area and distribution of zinc, cadmium, copper and nickel in mosses.

the background correction mode (deuterium lamp type), but background absorption was found to be insignificant.

Reagent blanks of the digestion process were analysed with each batch of 15 samples. The acids used for digestion were of analytical reagent (Analar) grade, while distilled water was double-distilled. Calibration working standards for atomic absorption analysis were prepared from the commercial BDH stock (1000) ppm solutions of the various metals, by diluting with 10% perchloric acid solution to closely match the matrix of diluted sample digests. Each sample was analysed in duplicate, and deviations ranging from 5–10% were obtained. The mean result for each sample is reported. A recovery study of the digestion and analysis steps was carried out by spiking five already-analysed ground moss samples with varying concentrations of metals. Each spiked sample was homogenised, redried, digested and analysed. The average recoveries obtained were lead $91.4 \pm 1.8\%$, copper $90.2 \pm 0.6\%$, nickel $94.1 \pm 2.4\%$, cadmium $88.6 \pm 4.1\%$, and zinc $94.2 \pm 1.1\%$. The results of metal concentrations were evaluated statistically using the Jandel Scientific SigmaStat 2.0 package.

RESULTS AND DISCUSSION

Concentrations of metals in roadside mosses in the northern and south-eastern regions of Nigeria are given in Tables I and II respectively, while a comparison summary of these results is given in Table III. Lead concentrations varied widely, ranging from 1.25 ppm to 327 ppm in

TABLE III Summary of results for moss metal concentrations (ppm) in both regions

Metal	*Parameter*	*Northern Region*	*South-eastern Region*	*Average for Entire Study Area*
Pb	Mean	44.4	58.8	–*
	Range	1.25–327	7.0–272	
Zn	Mean	38.2	60.7	50.9
	Range	11.6–189	12.5–319	
Cd	Mean	1.38	1.01	1.17
	Range	<0.02–4.6	<0.02–4.2	
Cu	Mean	12.4	10.4	11.3
	Range	4.0–79.5	2.1–68.8	
Ni	Mean	5.38	5.78	5.60
	Range	<0.05–16.5	<0.05–18.1	

*Difference between northern and south-eastern region is statistically significant.

the northern region. Average lead concentration for this region was about 44.4 ppm. Higher lead levels occurred predominantly in samples from the bigger towns such as Yola (327 ppm), Maiduguri (130 ppm), Abuja (92.1 ppm), and Kaduna (210 ppm). These are likely due to higher levels of emissions of automobile exhausts in such bigger towns. Lead content of Nigerian gasoline (0.6–0.8 g/l) ranks among the world highest. Moss lead levels in the south-east region were similarly widely varied (7.0–272 ppm; Table II), but were on the average (58.8 ppm; Table III) slightly higher than the levels in the north (Fig. 2). Using the non-parametric Mann–Whitney Rank Sum test, the difference in mean lead levels for both regions was determined to be statistically significant ($p = 0.044$). The south-eastern region is generally more industrialised and has a higher density of population concentrated in fewer towns

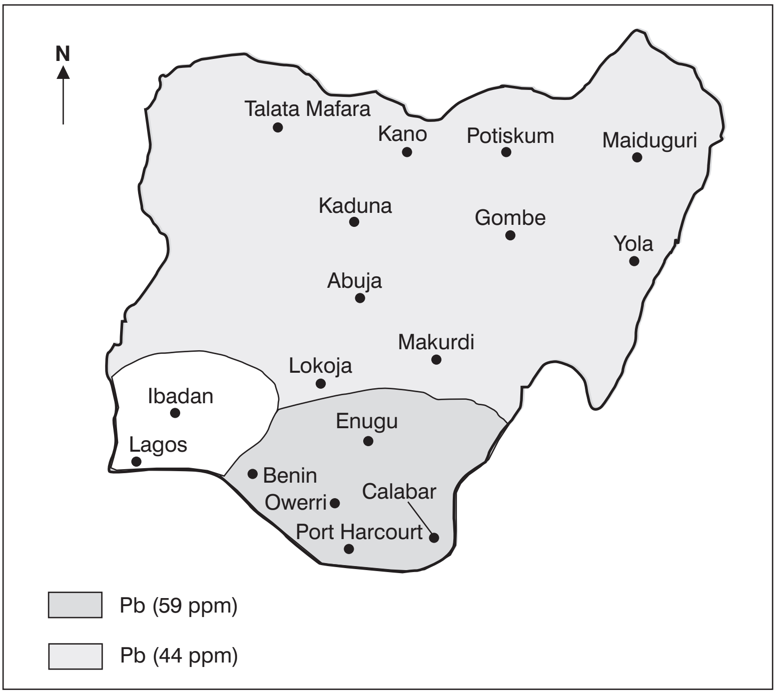

FIGURE 2 Distribution of lead in mosses in the study regions.

than is the case in the vast northern region. Automobile densities and emissions in the south-east towns are thus higher than in the north. Lead levels in the south-east samples were similarly mostly higher in relatively bigger towns: Umuahia (169 ppm), Owerri (84.0 ppm), Enugu (78.3 ppm) Port Harcourt (232 ppm), Aba (162 ppm), Benin (109 ppm), and Agbor (207 ppm). Lowest lead levels obtained in smaller towns of this region (about 8–10 ppm) are still indicative of a slight elevation above typical background levels. Natural background levels lower than 5.0 ppm have been obtained in similar species of mosses in remote forest sites (Onianwa *et al.*, 1986a). In the northern region, lead levels in some of the smallest towns were about this typical background value. Lead levels in mossess from both region are still well below levels which have been recorded for roadside mosses in some polluted sites elsewhere in the world, *e.g.*, Sweden: 700 ppm (Ruhling and Tyler, 1978); Louisiana, USA: 670–850 ppm (Martinez *et al.*, 1971; Nathany and Martinez, 1978). Levels in some of the bigger Nigerian towns however compare well with the 320 ppm that was found in roadside mosses in Manchester, UK (Lee, 1972).

Automobile emissions rather than dust contamination is believed to be the main source of elevation of lead above background levels in the moss. Whether or not moss metal concentration is significantly influenced by the substrate characteristics is still controversial. It is believed that the effect of substrate is particularly significant when the dust level of a metal is very much higher than the background level in moss, as is the case with elements such as calcium, magnesium and iron. In these cases, dust contamination may distort estimates of aerial uptake. For the trace heavy metals of interest however, studies mostly indicate that there is no significant effect of substrate concentrations on moss metal burden (Nagano, 1972; Huckabee and Janzen, 1975; Rasmussen 1978).

Zinc levels were well varied in both regions, with ranges of 11.6 ppm to 189 ppm in the north, and 12.5 ppm to 319 ppm in the south-east. The difference between average levels of 38.2 ppm in the north and 60.7 ppm in the south-east was determined from the Mann-Whitney Rank Sum test to be statistically insignificant ($p = 0.129$). Thus, the average zinc levels for both regions is better indicated by the overall average for the two regions, *i.e.*, 50.9 ppm (median = 33.4ppm) (Fig. 1). Zinc levels in both regions correlated very poorly with the lead values (Spearmann coefficients of -0.12 in the south-east, and -0.15 in the north). Zinc is associated in traces with automobile emissions in form of some zinc compounds used as additives in lubricants and from engine wear. However, contamination with zinc and other metals may also result from the burning of municipal solid wastes (Onianwa, 1994), and the operation of small metal works is a common practice in both regions. While the difference between the lead levels in both regions may be adduced to differences in automobile emission rates, the same cannot be said for the zinc levels. The lack of significant difference in regional averages for zinc, and poor correlation with lead indicate that random sources such as refuse burning may also be significant in determining the zinc levels. Background zinc levels in Nigerian mosses are typically about $<$ 10–20 ppm (Onianwa *et al.*, 1986a).

Cadmium levels in the moss samples were low, with many of the sites having levels below 0.02 ppm. Average cadmium level of 1.38 ppm in the northern region is not significantly different from the 1.01 ppm for the south-east ($p = 0.397$). Thus, no zonation is discernible in the distribution of cadmium in the mosses, and the overall average for the entire study area was estimated to be 1.2 ppm (Fig. 1). Background cadmium levels in remote forest mosses are typically $<$ 0.02 ppm. Cadmium levels were similarly very poorly correlated with the lead levels ($r = -0.177$ for the north; -0.186 for the south-east). Thus, the slight elevation of cadmium concentrations above natural background values in some samples may derive from sources other than automobile emissions.

TABLE IV Summary of the concentrations of the metals in roadside moss samples from the south-west region of Nigeria (Onianwa and Ajayi, 1987)

Zones		*Pb*	*Zn*	*Cd*	*Cu*	*Ni*
Higher Pollution	Mean	136 ± 77	99 ± 34	0.35 ± 0.21	26.3 ± 6.0	10.2 ± 2.7
	Range	26.7–281	53.4–153	<0.05–0.70	17.4–38.1	5.2–13.5
Medium Pollution	Mean	42 ± 19	150 ± 110	0.16 ± 0.17	17.8 ± 4.8	8.0 ± 2.3
	Range	12.4–127	31.6–496	<0.05–0.77	8.1–29.7	3.6–15.7
Low Pollution	Mean	14.3 ± 7.5	70 ± 34	0.12 ± 0.15	14.1 ± 6.2	7.0 ± 2.3
	Range	6.6–33.3	26.3–140	<0.05–0.65	8.1–30.9	3.5–13.5

The distribution patterns for copper and nickel were similar to those for zinc and cadmium, with averages for the northern region being not statistically different from those for the south-east. The grand averages for the study area were: copper—11.3 ppm; nickel—5.6 ppm (Table III, Fig.1). Both metals were also poorly correlated with lead. Natural background concentrations in Nigerian mosses is typically < 10 ppm for copper, and < 6 ppm for nickel (Onianwa *et al.*, 1986a). Both metals are thus not much elevated above the background values.

Table IV is extracted from the summarised data of the similar study of the south-west region using roadside mosses (Onianwa and Ajayi, 1987). In that study, it was possible to map sub-regional zones in levels of some of the metals because the most contaminated towns appeared to be congregated within the same area. This is not the case in the present study of the north and south-east where the few more contaminated towns are not localised to a particular area of each region. The average levels of lead in both regions were significantly lower that the 136 ppm which was recorded for the most polluted areas of the south-west. The levels of lead rather compared well with the 42 ppm observed for the moderately polluted parts of the south-west.

Average zinc and copper levels in the south-west samples appeared to be higher than average levels in the north and south-east. Cadmium levels were generally higher in the samples from the two regions than in samples from the south-west. Nickel levels in the north and south-east compared well with levels found in low pollution zones of the south-west. Generally, the northern and south-eastern regions appeared to be less polluted than the south-west region. This may be expected because the south-west region is generally more industrialised than the other regions, with 60% of all industries in Nigeria located in the south-west.

Acknowledgment

The participation of Professor Gary van Loon of the Department of Chemistry, Queens University, Kingston, Ontario, Canada, in the sampling programme is gratefully acknowledged.

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