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LEVELS OF HEAVY METALS IN OWL'S FEATHERS AND ATMOSPHERIC POLLUTION

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Birds feathers act as traps for toxic and heavy metals present in the atmosphere and indicate levels of pollution in the living area of the bird. Different metals (Cd, Pb, Cu, Zn, Ni and Co) have been analysed in Owl's feathers. Studies have been done concerning distribution of metals in upper and lower parts of the feather. Upper parts of feathers have higher concentrations of metals as compared to lower parts except for Zinc. Feathers of Owls caught from polluted and unpolluted areas have been analysed. Comparative studies have been done between the rain water samples and birds feathers collected from polluted and unpolluted areas. Metal ratios for polluted to unpolluted areas for rain water samples and birds feathers are in good agreement with each other. Upper half of the feather is a better indicator for atmospheric pollution than the lower half.

Key words: Heavy metals, Biomonitoring, Feathers, Owl, Voltammetry.

Introduction

Analysis and monitoring of metals in different environmental systems is important, because certain metals (Cd, Pb, Hg) are toxic even at trace levels [1,2]. Some other metals are essential at trace concentrations and become toxic after certain threshold levels [3,4]. Most of the metals and metalloids are not biodegradable but undergo a biogeochemical cycle during which only transformations into more or less toxic species occur. Metals and metalloids have a special characteristic which is to accumulate over long exposure times. The most important pathway for intake of these metals by human beings is through food. The entrance of these metals into the different food chains, is through the atmosphere. Thus monitoring of the atmosphere for pollution through different toxic metals is necessary. One of the most important methods for monitoring metals in the atmosphere is through anslysis of rain water samples. Considerable amount of work has been done over the wet deposition of metals from the atmosphere [5-7]. It has been reported [8] that birds can be used successfully as integrated bioindicators for environmental pollution by metals. To get meaningful data from birds feathers about environmental pollution, the bird selected must have a fixed living area and other parameters e.g. bird's age and food habits must be known and one must know the distribution of metals in birds feathers to find out the parts of feathers which are true representatives for atmospheric pollution.

In this work the bird selected was Owl, which is well known for its fixed living area of 2-3 km^2 [9]. Studies about the distribution of metals in different parts of the feathers were done. Comparative studies have been undertaken between the birds feathers and rain water samples taken from polluted and unpolluted areas.

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Experimental

Chemicals. All acids were of suprapure grade from E. Merck. Standard solutions containing 1 g/l of metals were prepared from E. Merck, titrisol and deionized water from a Milli-Q-purification system. Further diluted standard solutions were prepared in 0.2% HCl, NH_3 used was of suprapure grade from E. Merck. Dimethylglyoxime (DMG) used was of p.a. quality also from E. Merck.

Apparatus. Quartz glass crucibles of about 25 ml volume were used for digestions and were covered with watch glasses. Titanium scissors were used from cutting purposes. All the glassware used was quartz or pyrex. Precleaned polyethylene gloves were used from sample preparation and measurements.

Polarographic analyzer used was Model 384B of Princeton Applied Research (PAR), U.S.A. with a plotter DMP-40 series digital plotter of Bausch and Lomb, Houston instruments, U.S.A. Hanging mercury drop electrode used with polarographic analyzer was Model 305 of PAR, U.S.A.

Procedure. The desired feathers were taken out carefully, washed with acetone, dried and cut into small pieces. Feathers were cut with titanium scissors. Required pieces were weighed and transferred into quartz crucibles. About 1.0 ml HNO_3 and 0.25 ml perchloric acid were added to the crucible and that was then covered with watch glass. The digestion was done initially at low temp. and then at higher temp. [10]. The digestion of birds feathers is relatively easy than many other biological materials [11]. After the digestion volume was made to 10 ml with deionized water. 5.0 ml of 0.04 N $HClO_4$ were taken in the cell as background electrolyte. 0.1–0.5 ml of the sample solution was added to the background electrolyte and measured for Zn, Cd, Pb and Cu by anodic stripping square wave voltammetry. For Ni and Co background electrolyte used was NH_3/NH_4Cl buffer at pH 9.2 and $1x10^{-4}M$ dimethylglyoxime and measurement was done using adsorptive square wave voltammetry.

Results and Discussions

Voltammetry is a very sensitive and reliable analytical technique [12,13]. Digestion and measurement procedures were throughly investigated before starting the actual measurements in feathers. Owls feathers were taken from Stolberg and Julich, Germany (State Nordrhein-Westfalen). Ages and sexes of the Owls were determined carefully. In Fig.1 are shown different feathers of a bird. P is for primary feathers which are 1–10 and S is for secondary feathers which are also 1–10. T is for tail feathers which are 1–6. R and L with numbers show the number of feather on the right or left side of the bird when seen from the back. In Fig.2 LF means lower half of the feather and UF means upper half of the feathers. Here only the feathers were taken without the quill for measurements.

Distribution of metals in feathers. In Table 1 is shown the distribution of metals in the upper and lower halves of the feather vertical to the quill. Feathers taken are from the tail, primaries and secondaries. Normally the concentration of Zn is slightly higher in the lower half of the feather as compared to the uper half. Concentrations of other metals are appreciably more in the upper half of the feather as compared to the lower half and the concentrations of the metals in the lower half are 40–45% for all the elements i.e. Cd, Pb, Cu, Ni and Co as compared to the concentrations of metals in the upper half, but the concentration of Zn is less in the upper half and is about 85% as compared to the lower half. Here the behaviour of Zn is different as compared to the other metals. These feathers were taken from a male bird caught from relatively unpolluted area. Here feather means only webb of the feather without quill, because the detailed studies have shown that quill is not a good representative of environmental pollution [14].

Comparison between bird's feathers from polluted and unpolluted areas. For comparative purposes one must know all the necessary details about the birds and only the same species with similar age and other similar parameters and the same feathers can be used. In Table 2 are given the concentrations of metals in birds feathers caught from unpolluted area (Julich) and more polluted area (Stolberg). Feathers of birds from polluted area contain much more concentrations of metals than from unpollutd area. Increase in Zn, Ni and Co is nearly 4 times while that in Cd, Pb and Cu is nearly 15 times in samples from polluted area than in samples from unpolluted area. Both of these birds were male and their age was about two years i.e. 1982–1983. Same tail feathers of both the birds were compared.

Comparison between rain water samples from polluted and unpolluted areas. Data about the concentrations of metals in rain water samples from unpolluted area (Julich) and polluted area (Stolberg) was available [15]. In Table 3 are shown the metal concentrations in rain water collected from Julich and Stolberg areas. From Stolberg area rain water samples were collected from two points i.e. Stolberg (Werth) and Stolberg (Binsfeldhammer). As both of these areas are between two kilometers area, therefore values from both of these areas are added together and averaged out to give a representative values for Stolberg area within a radius of 2–3 Kilometers. Ratio between the metal concentrations from Stolberg and Julich areas have also been calculated in Table 3, which gives the degree of pollution of Stolberg area as compared to Julich area.

Bird's feathers as integerated biomonitors for environmental pollutions. If the birds feathers are indicators of environmental pollution, then the ratio of trace elements in polluted and unpolluted areas in rain water samples should

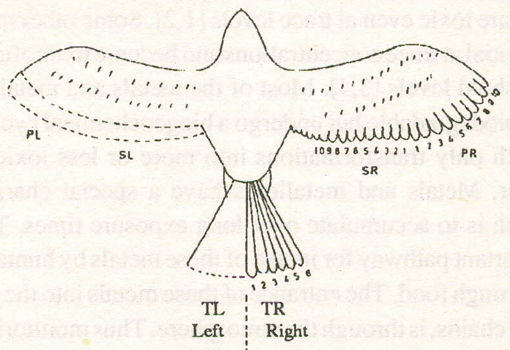

Fig. 1. Terminology used for feathers, P is for primary, S for secondry and T for tail feather, L is for left and R is for right.

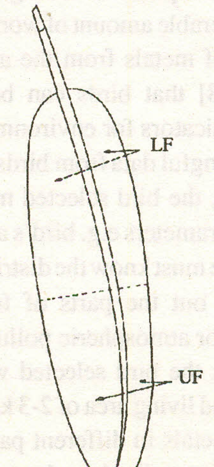

Fig. 2. Parts of feather: LF is lower half of the feather, UF is upper half of the feather.

correspond to the ratio of trace elements in birds feathers from polluted and unpolluted areas. In Table 4 are compared the metal concentration ratios between Stolberg area (polluted) and Julich area (unpolluted) both for rain water samples and birds feathers. It can be seen that the ratios of metal concentrations in rain water samples are nearly similar to ratios in upper halves of feathers for Cd, Cu and Zn but for Pb the variation is nearly 50%. For Pb the reason may be that major part of Pb is not dissolved in rain water, if Pb is present in the atmosphere as a compound of sulfur or $PbSO_3$. Due to the presence of large quantities of sulfur and sulfur compounds in the atmosphere, lead may certainly exist in the atmosphere in the form of water insoluble compounds. Even if these compounds are washed down with rain into rain water samplers, these remain in the

TABLE 1. DISTRIBUTION OF METALS IN THE UPPER AND LOWER PARTS OF THE FEATHERS VERTICALLY TO THE QUILL.

S.	Sample	Zn (μg/g)		Cd (μg/g)		Pb (μg/g)		Cu (μg/g)		Ni (μg/g)		Co (μg/g)	
No.	No.	UF	LF	UF	LF	UF	LF	UF	LF	UF	LF	UF	LF
1.	TR$_1$F	95.32	185.84	1.40	1.04	17.59	8.67	8.40	4.68	1.035	0.663	0.366	0.233
		±1.30	±9.67	±0.03	±0.04	±0.01	±0.05	±0.42	±0.25	±0.01	±0.03	±0.02	±0.002
2.	TR$_4$F	161.89	203.63	1.58	0.699	17.81	13.65	13.65	6.03	6.78	2.50	1.454	0.597
		±1.0	±6.76	±0.14	±0.06	±1.31	±0.01	±1.61	±0.28	±0.18	±0.17	±0.005	±0.07
3.	PR$_2$F	165.43	172.47	1.044	0.576	28.37	11.88	12.48	4.57	4.16	1.15	0.608	0.354
		±2.1	±6.76	±0.05	±0.0	±1.31	±1.09	±1.02	±0.23	±0.32	±0.06	±0.10	±0.004
4.	PR$_4$F	181.08	169.4	0.99	0.449	45.69	12.36	15.25	4.14	4.20	1.34	0.782	0.342
		±1.8	±2.04	±0.09	±0.038	±0.67	±0.62	±0.26	±0.24	±0.01	±0.17	±0.15	±0.03
5.	PR$_6$F	130.94	155.99	0.738	0.117	12.10	2.60	4.39	2.22	1.47	0.307	0.471	0.167
		±1.18	±4.58	±0.05	±0.007	±1.16	±0.06	±0.01	±0.07	±0.08	±0.03	±0.03	±0.02
6.	PR$_8$F	143.05	186.21	1.70	0.774	39.08	20.61	11.41	4.59	7.08	3.01	1.50	0.581
		±1.9	±6.43	±0.08	±0.03	±1.36	±0.9	±1.07	±0.08	±0.01	±0.19	±0.05	±0.05
7.	SR$_4$F	186.00	190.23	0.99	0.446	29.49	10.33	12.64	6.49	2.39	1.64	0.386	0.322
		±1.7	±3.98	±0.005	±0.006	±0.94	±0.02	±1.06	±0.19	±0.14	±0.06	±0.02	±0.03

TABLE 2. CONCENTRATIONS OF METALS IN BIRDS FEATHERS FROM POLLUTED (STOLBERG) AND UNPOLLUTED (JULICH) AREA.

S.No.	Sample	Zn (μg/g)	Cd (μg/g)	Pb (μg/g)	Cu (μg/g)	Ni (μg/g)	Co (μg/g)
1.	Julich TR$_1$F						
	Lower feather	303.1±2.2	0.78±0.5	16.53±0.04	7.1±0.5	1.57±0.02	0.67±0.11
	Upper feather	243.1±1.5	1.47±0.01	39.4±2.8	13.05±1.2	3.68±0.3	0.81±0.09
2.	Stolberg TR$_1$F						
	Lower feather	370.6±13.7	6.15±1.35	314.2±51.5	51.28±11.05	2.02±0.27	0.73±0.02
	Upper feather	800.2±44.4	18.47±0.54	665.61±9.3	201.7±4.99	14.3±0.48	4.15±0.03

TABLE 3. AVERAGE DAILY WET DEPOSITION OF METALS IN POLLUTED AND UNPOLLUTED AREAS.

Element	Stolberg Werth		Stolberg Binsfeld-hammer		Julich		Stolberg Werth + Binsfeldhammer (average)	
	1982	1983	1982	1983	1982	1983	1982	1983
Cd	2.4	2.1	9.7	12.5	0.54	0.5	6.05	7.3
Pb	130	85	450	340	38.0	25.0	290.0	212.5
Cu	27	25	120	100	5.7	3.5	73.5	68.5
Zn	86	99	200	170	31.0	49.0	143.0	134.5

TABLE 4. RATIOS BETWEEN POLLUTED AND UNPOLLUTED AREAS FOR BIRDS FEATHERS AND RAIN WATER AND THEIR COMPARISON.

Element	Ratio of polluted(Stolberg)/unpolluted (Julich)				
	Bird's feathers			Rain water	
	Lower half	Upper half	Full	1983	Average of 1982+83
Cd	7.84	12.52	11.4	14.60	12.90
Pb	19.01	16.89	17.34	8.50	8.06
Cu	7.23	15.45	13.48	17.86	15.37
Zn	1.22	3.29	2.41	2.74	3.67

undissolved residue and do not dissolve in rain water due to the low acid concentrations used in rain water collection and sample preparation [15]. It has also been shown [16] that increased concentrations of acids increase the recovery of metals from rain water.

Now trace elements and their compounds get adsorbed on the feathers from the atmosphere and the wet digestion methods used here will bring all lead compounds into solution form. Due to these reasons birds feathers may contain higher concentrations of lead as compared to rain water samples, thus enhancing the polluted to unpolluted ratio for lead in birds feathers considerably. In Table-4 are also compared the ratios of trace elements in birds lower, upper and full feathers between polluted and unpolluted areas, values in low half feathers do not agree with rain water samples and values for full feathers are near about but the values for upper half feathers agree well with the rain water samples. Thus one can conclude that upper half feathers may be used for monitoring atmospheric pollution. But lower halves of the feathers cannot be used and complete feathers are also not as good representative as the upper halves of the feathers. The reason may be that during flight upper halves of feathers are more exposed to the atmosphere as compared to the lower halves [17].

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