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Evaluation of efficacy of bricks as geochemical monitor of atmospheric heavy-metal pollution

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Geochemical monitoring of atmospheric heavy-metal pollution is so far limited to the use of peat, ice deposits and aquatic sediments as sample type. These systems are open, dynamic and easily affected by climatic variations. In contrast, bricks, which are more compact, can act as a better geochemical monitor. Heavy-metal (Cu, Zn, Ni, Cr, Pb) analysis in scores of soil and baked/unbaked brick samples collected from a large area in and around Agra City indicates approximately similar flux in soils and bricks and insignificant fractionation during brick construction of these metals. The concentration of analysed metals in the core of bricks remained unaffected even by substantial amounts of acidic/alkaline rain under natural conditions. Thus, the feasibility of a new, hitherto untested, concept of bricks acting as a geochemical monitor of atmospheric heavy-metal pollution has been systematically explored.

ATMOSPHERIC heavy metals interact with terrestrial environment continuously. From the standpoint of mass,

their major amount is absorbed by plants and soils^{1,2}. Chronological changes in the heavy-metals flux of terrestrial objects, mainly as a result of atmospheric depositions, reflect the impact of human growth on accumulation of toxic metals on the global ecosystem over the years. Studies of the practical applications of geochemical monitoring have been carried out mainly in Northwest Europe, North America and the remote polar regions, particularly in relation to the historical aspects of pollution. Records from peat deposits and lake sediments in Europe document the growth and development of industry there over the last 2000 years³⁻⁸. Reconstructed historical deposition rates demonstrate the severity of pollution in urban areas of northern Britain in the eighteenth and nineteenth centuries, whereas analysis of recent sediments reveals a variable pattern of present-day pollution, with some areas experiencing increasing levels of deposition and others decreasing ones⁹⁻¹¹. In North America deposition records reveal a much shorter history of atmospheric pollution and document the rapid spread of heavy metals during the mid and late nineteenth century, both on a local and on a regional scale¹²⁻¹⁶. For most of the other parts of the world, no such detailed information exists and studies are limited mainly due to lack of suitable sample types, where the original heavy-metals compositions remain preserved unperturbed over long periods of time. Peat, ice deposits and aquatic sediments, most extensively used so far in monitoring the atmospheric depositions of heavy metals are open, dynamic systems and can be easily affected by climatic changes.

The use of baked bricks in the construction of buildings is an age-old practice all over the world. The commercial process of construction and baking of bricks has not changed much over the years, and the stuff used in brick manufacture is primarily soil derived from the top 1-1.5 m of the earth, a portion where atmospheric depositions of heavy metals are most likely to be retained². The temperature of bricks during commercial baking rises up to $\approx 700^\circ\text{C}$, at which most of the soil-bound heavy metals possibly remain intact in soil matrix. Hence, bricks of any specific period of time, if kept preserved from the effects of rain and radiations, can be regarded as representative samples of soil of that period, from the viewpoint of heavy-metals composition. Bricks, which can be effectively used for chronological monitoring of atmospheric heavy-metal depositions in soil and which are likely to be better than so far used sample types, viz. ice, peat and sediments, have eluded the attention of researchers till now. This paper deals with a systematic evaluation of the effectiveness of bricks for this purpose.

From an approximately 10^3 km^2 area in and around Agra City the following samples were collected: (i) baked and unbaked (65 each) brick samples from

different brick kilns; (ii) bulk soil samples from 35 places after removing the top 7–10 cm layer of the earth; (iii) bulk soil samples from 5 places (wide apart) after every 30 cm depth (up to 1.5 m). The soil samples were air-dried (at 35°C), mildly ground and mixed well; the texture of few representative samples was determined by the wet sieving procedure. The inner core (≈ 50 g) of each brick sample was taken out by removing the external layers in a mechanical cutter and ground to powder form avoiding external contaminations. The grinding was done till the final texture of the brick powder was almost identical to the texture of the soil. The acid extracts of powdered brick and soil samples, generated under mild, semidrastring and drastring acid treatments (detailed below), were quantitatively analysed for Cu, Zn, Ni, Cr and Pb using the standard methods¹⁷, employing Perkin Elmer 2380 flame atomic absorption spectrometer at appropriate wavelengths.

For mild treatment the sample (6 g) was treated with 10 ml HCl (3 M) and 10 ml HNO₃ (3 M) for 24 h and then boiled till the volume was reduced to 3–5 ml. After adding 20 ml of 0.01 M HCl, the contents were further heated for 15 min, cooled, filtered through acid-washed Whatman 42 filter paper and the extract was collected for analysis.

For moderate treatment the sample (6 g) was treated, in a teflon vessel, with 10 ml HCl (6 M), 10 ml HNO₃ (6 M) and 1 ml HF (48%) for 24 h, followed by slow heating at 45–60°C till the volume was reduced to 3–5 ml. In order to ensure the complete removal of unreacted HF, 20 ml of 0.1 M HCl was added and the contents were further heated at elevated temperature (65–80°C) till the volume was again reduced to 3–5 ml, which was then transferred to a glass vessel using 20 ml of 0.01 M HCl as the washing solution. The contents were boiled till the volume was reduced to half, cooled, filtered as above and the extract was collected.

For drastring treatment the sample (6 g) was treated, in a teflon vessel, with 5 ml HCl (12 M), 5 ml HNO₃ (16 M) and 10 ml HF (48%) for 24 h and then heated gently at 45–60°C till the volume was reduced to 3–5 ml. Adding 5 ml each of HCl (12 M) and HNO₃ (16 M), the contents were further heated at 65–80°C till the volume was again reduced to 3–5 ml. At this stage the complete removal of unreacted HF was ensured. Using 20 ml of water as the washing solution, the contents were transferred to a glass vessel, boiled till the volume was reduced to half, cooled, filtered as above and the extract was collected.

The final volume (after washings) and pH of all the extracts were adjusted, respectively, to 50 ml and 3–4 by suitable additions of HCl (0.01 M), NaOH (0.01 M) and water. Metal concentrations were determined in reagent-blank extracts also and the values were subtracted from the main data. The extract samples were stored

in acid-washed polythene bottles before analysis. Double-distilled deionized water and AR grade reagents were used throughout the study.

The textures of 20 randomly chosen samples each of powdered bricks and soils were determined (Table 1). The results indicate approximate similarity of the two systems. The average concentrations of Cu, Zn, Ni, Cr and Pb in soil and baked/unbaked brick samples, as determined by the analysis of extracts generated under mild, moderate and drastring treatments, are presented in Table 2. Table 3 shows the results of some laboratory experiments to observe the effects of rain (of varying pH) on heavy-metal concentrations in the core of baked bricks while the bricks are exposed to natural conditions at 30–35°C.

Soil concentrations of metals are in the range of earlier reported values of some Indian soils¹⁸. Extracts of soil and brick samples generated through mild and moderate extraction procedures show a wide variation in their metal concentrations, whereas drastring-treatment data indicate approximately similar concentrations of metals in soils and baked/unbaked bricks. It is also clear that except for Cr, which shows a slight increase, the concentrations of the remaining four metals in soils of the studied area are not significantly changing with depth (ranging from 0.1 to 1.5 m). Metal concentrations in the core of baked bricks remain unaffected by substantial amounts of acidic/alkaline rain and radiations. However, prolonged exposure of bricks to these results in some changes.

The close association of soil-bound heavy metals with soil matrix, largely composed of silicates, is well known and might further increase during brick construction, depending upon the maximum temperature reached during baking. Hence, determination of metal concentrations in soil and brick extracts depends on the effectiveness of the extraction technique in breaking/dissolving the soil matrix. The wide range of fluctuations in data (Table 2) under mild and moderate treatments indicates inadequacy of extraction procedures in breaking the matrix, and only the drastring treatment, with 95–100% dissolution of the sample, seems to give satisfactory results.

The temperature of bricks during commercial baking

Table 1. Texture of powdered brick and soil samples

Particle size (mm)	Percentage amount*	
	Soil	Powdered brick
60-2	0.36-0.42	0.41-0.49
2-0.2	36.13-40.50	38.10-43.21
0.2-0.06	27.91-34.12	31.63-39.00
0.06-0.006	14.93-19.23	11.54-16.24
0.006-0.002	3.04-7.33	3.02-7.10
< 0.002	3.52-10.10	1.09-6.25

*Based on measurements in 20 randomly chosen samples

Table 2. Mean concentration (mg kg⁻¹) of metals in soil and brick samples

Extraction technique		Concentration				
		Cu Mean ± SD	Zn Mean ± SD	Ni Mean ± SD	Cr Mean ± SD	Pb Mean ± SD
Drastic	*(0.07-0.1)	1.9 ± 0.15	4.8 ± 0.39	5.9 ± 0.49	3.6 ± 0.33	5.0 ± 0.45
	*(0.3)	2.0 ± 0.22	5.0 ± 0.40	5.8 ± 0.50	3.8 ± 0.35	4.9 ± 0.50
	*(0.6)	1.9 ± 0.18	4.7 ± 0.35	6.2 ± 0.50	3.9 ± 0.30	5.1 ± 0.45
	*(0.9)	2.2 ± 0.19	4.8 ± 0.35	6.3 ± 0.49	4.2 ± 0.32	5.1 ± 0.50
	*(1.2)	2.1 ± 0.20	4.9 ± 0.37	5.9 ± 0.48	4.6 ± 0.30	5.2 ± 0.40
	*(1.5)	2.0 ± 0.17	4.9 ± 0.37	5.9 ± 0.51	4.6 ± 0.33	5.0 ± 0.44
	†	2.1 ± 0.19	4.8 ± 0.40	6.3 ± 0.50	3.9 ± 0.35	5.2 ± 0.50
	‡	2.0 ± 0.21	4.8 ± 0.38	6.0 ± 0.49	4.0 ± 0.33	4.8 ± 0.46
Moderate	*(0.07-0.1)	1.9 ± 0.81	3.9 ± 1.28	4.2 ± 1.83	2.3 ± 1.52	2.9 ± 1.79
	†	1.4 ± 0.93	3.0 ± 1.35	3.6 ± 1.64	3.3 ± 1.69	3.5 ± 1.92
	‡	1.1 ± 0.80	2.6 ± 1.44	3.7 ± 1.53	2.9 ± 1.67	2.5 ± 1.84
Mild	*(0.07-0.1)	0.8 ± 0.32	0.9 ± 0.71	1.2 ± 0.87	0.9 ± 0.76	1.5 ± 0.89
	†	0.6 ± 0.41	0.7 ± 0.63	0.9 ± 0.80	1.3 ± 0.66	1.1 ± 0.92
	‡	0.4 ± 0.33	1.2 ± 0.94	1.3 ± 0.91	0.8 ± 0.78	0.9 ± 0.81

*Soil; †unbaked bricks, ‡baked bricks.

Values in parenthesis represent depth in m, from top, at which the sample was collected.

Table 3. Mean concentration (mg kg⁻¹) of metals in the core of baked bricks, after their exposure to intermittent simulated rain (100 ml day⁻¹) under natural conditions at 30–35°C (drastic-treatment data)

Rainfall		Concentration*				
Duration in days	pH	Cu Mean ± SD	Zn Mean ± SD	Ni Mean ± SD	Cr Mean ± SD	Pb Mean ± SD
2	7.5	2.2 ± 0.17	4.9 ± 0.40	6.2 ± 0.50	3.9 ± 0.33	5.1 ± 0.43
5	7.5	2.3 ± 0.19	4.7 ± 0.37	6.0 ± 0.51	3.9 ± 0.35	5.1 ± 0.47
10	7.5	2.0 ± 0.18	4.8 ± 0.39	5.9 ± 0.47	3.5 ± 0.31	4.9 ± 0.46
2	6.0	2.0 ± 0.21	4.8 ± 0.35	6.0 ± 0.48	4.0 ± 0.34	5.2 ± 0.50
5	6.0	2.2 ± 0.22	4.6 ± 0.37	6.2 ± 0.51	3.8 ± 0.35	5.1 ± 0.48
10	6.0	1.9 ± 0.22	4.5 ± 0.41	6.1 ± 0.49	3.5 ± 0.33	4.8 ± 0.49
2	5.0	2.1 ± 0.19	4.9 ± 0.41	5.9 ± 0.47	4.1 ± 0.35	5.1 ± 0.50
5	5.0	1.9 ± 0.22	4.6 ± 0.39	5.8 ± 0.50	3.8 ± 0.35	4.8 ± 0.50
10	5.0	1.9 ± 0.21	4.4 ± 0.41	5.6 ± 0.50	3.6 ± 0.34	4.6 ± 0.51

*Average of 40 samples.

rarely exceeds 700°C, and the existing vaporization/dissociation temperature data¹⁹ of different metal salts suggest that the major amount of most of the soil-bound heavy metals possibly remains intact in the soil matrix at this temperature. This contention is supported by drastic-treatment results (Table 2), indicating approximately similar concentrations of metals in soils, unbaked bricks and baked bricks. The negligible fractionation of metals during brick construction and to some extent insignificant effect of rain and radiation on heavy-metal concentrations in the core of bricks (Table 3) make it feasible to consider bricks as representative samples of the parent soil from the viewpoint of heavy-metals composition. The compactness and easy availability are other distinct advantages in using bricks as a geochemical monitor, rather than ice, peat and sediments.

From the viewpoint of plant nutrition, soil layers at 0.1–1m depth from the top are the most important

because mineral-absorbing zones of plant roots generally lie in this region. Changes in concentrations and mobility of metals in this region have a direct consequence on the living systems, and the entry of some toxic metals in the food chain cannot be ruled out. Incidentally, in brick construction also, this portion of soil is mainly used. Thus, bricks act not only as representative samples of the parent soil but also as samples of biologically most important layers of the top soil.

Heavy metals enter the soil through many sources, viz. atmospheric depositions, agricultural activities, industrial and local emissions. By analysing bricks of different ages derived from interior and well-preserved portions of old buildings/monuments for different metals and presenting the data on time scale, it is possible to trace the past and present accumulation rates of metals in soils of a particular area. Moreover, with the help of statistical tools the identification of probable sources of these metals and the estimation of their contributions

is possible. Analysis of samples collected from remote areas, where local effects are negligible, will reflect the rates of global inputs through atmospheric depositions. In contrast to approximate and lengthy stratigraphic, biostratigraphic, radiometric and geomagnetic techniques used for dating aquatic sediments, peat and ice deposits, the dating method for bricks is limited to determining the construction time of the building from which the brick sample is derived. Most parts of the world have witnessed much of the industrial and urban growth only during the last 200 years and brick samples of this duration can be easily obtained and accurately dated. Further, bricks being heavy construction material are never transported over long distances due to economic reasons and remain representative samples of soil of the area of their collection.

Though our study has shown both bricks and soil as true representatives of each other in respect of concentrations of all the five metals analysed, this trend, far from being general, is bound to be dependent on soil characteristics of the particular area and minor variations in brick-making process from place to place. In the event of certain metals showing considerable fractionation during brick construction, the ratio x ($x = [\text{metal}]_{\text{soil}} / [\text{metal}]_{\text{baked brick}}$) may be determined by analysing a large number of present-day samples. With some approximations, the average values of x (for different metals) can be utilized in calculating metal concentrations in soils of different ages from the metal concentrations data of old bricks. The present study, thus, leads to the following conclusions:

1. From heavy-metal concentrations viewpoint, except for few volatile metals, bricks derived from interior and well-preserved parts of buildings can be regarded as representative samples of the parent soil.

2. To some extent, rains and radiations do not change metal concentrations in the core of bricks.

3. Due to greater compactness and easy availability of samples, bricks are likely to be a better geochemical monitor than ice, peat and sediments and can be used in geochemical monitoring of heavy-metal pollution. However, this technique has to be used judiciously for monitoring atmospheric heavy-metal pollution of soil in historical times due to anthropogenic activities in the

past, because the parent soil of a brick collected from a specific area may have inherently high heavy-metal content due to natural causes also.

Finally, it should be stated that the conclusions derived here are based on the study restricted to the city of Agra and its suburbs only. More such studies, in other parts of the world, are needed to understand the exact potential of bricks as a geochemical monitor.

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