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The Absorption of Arsenic into Single Human Head Hairs

The study of arsenic in human head hair has long been of considerable interest as a potential index of arsenic poisoning. Two accounts are found in the literature of the mechanism by which arsenic becomes desposited in hair. In one, ingested arsenic is incorporated into the growing hair shaft via the follicle [1]; the location at specific distances from the hair root of regions of increased concentrations of arsenic in hair taken from subjects after the ingestion of arsenic [2] (for example, from Napoleon Bonaparte at various times before his death [3,4]) were interpreted as indicative of the time before plucking at which arsenic ingestion had occurred, under assumptions as to the rate of growth of hair.

A second mechanism, perhaps operating in conjunction with the first, involving transport down the hair by sweat or during hair washing, is indicated by experiments by Lima [5]; also, previous studies in this laboratory [6,7] have revealed that highly structured concentration patterns for copper and zinc can arise when these elements are absorbed by individual hair shafts from externally applied solutions.

The present paper describes work aimed at determining whether structured concentration patterns also arise when arsenic is absorbed from external sources. Information was also sought on the distribution of arsenic-binding sites for comparison with that previously obtained for binding sites for copper and zinc.

Experimental Techniques

Hairs were plucked from the heads of subjects, described in previous publications [6,7], via techniques designed to reduce contamination (which might affect absorption of ions from solution). After plucking, hairs were selected which were in the anagen phase of the hair growth cycle as determined by microscopic examination of the hair root. The selected hairs were then washed to remove superficial material with the ether-acetone-water cycles described previously [6]. Washing times were 5 min per step.

Radioactive arsenic tracer solution was prepared by irradiation of a weighed quantity of arsenic trioxide with neutrons in the University of Washington (Seattle) reactor to a specific ⁷⁶As activity of 0.21 mCi/mg. After irradiation, the arsenic trioxide was dissolved in 1*N* sodium hydroxide solution to give an arsenic concentration of 0.58 mg/ml, and the pH of the solution was adjusted to 5.5 by adding hydrochloric acid. The pH value was chosen to be the same as that used in the copper and zinc absorption experiments.

The hairs were individually soaked in this solution for the lengths of time indicated below, and then rinsed with water, acetone, and ether for one min each to remove adhering

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tracer solution. After air drying, the hairs were individually cut into 2-mm long segments under microscopic observation and by means of the techniques described previously [6, 7]. The segments were each mounted onto aluminium planchets, and the arsenic radioactivity was assayed by conventional beta-counting equipment. The radioactivity data were converted to masses of arsenic absorbed via similar measurements made from time to time in the assay sequence on samples prepared by evaporation of aliquots of known volume of the original arsenic tracer solution.

Results

A hair from Subject A was soaked for 22 h by the above techniques. The resulting pattern of radioactivity uptake is shown in Fig. 1, together with the pattern of zinc uptake

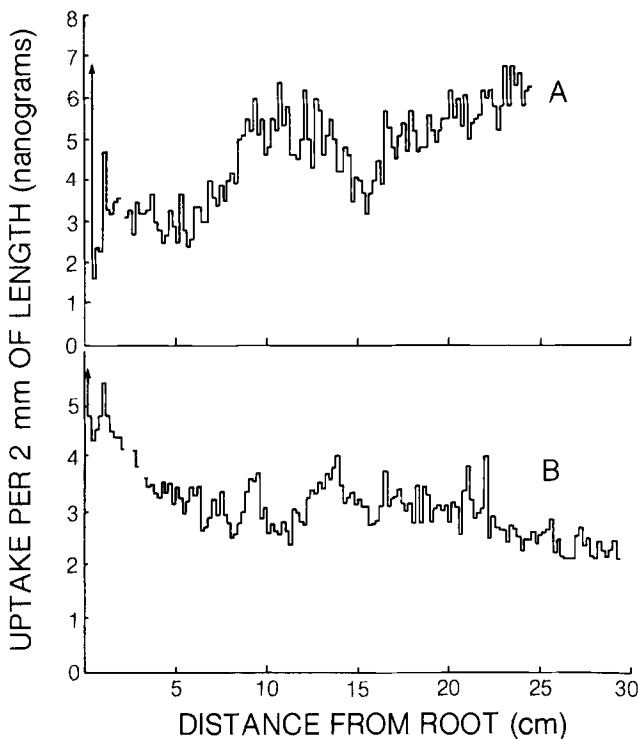


FIG. 1—Element absorption patterns for hairs from Subject A; (A) pattern for zinc absorption (reproduced from Ref 7) and (B) pattern observed for radioarsenic uptake after soaking in tracer solution for 22 h.

observed in a second hair plucked at the same time (reproduced from a previous paper [7]). The zinc pattern is similar to those reported earlier [6] for copper for this same subject and shows a concentration of absorbed zinc generally increasing with increasing distance from the root, but with regions near 10 and 20 cm from the root of locally greater values. The arsenic pattern, however, shows a concentration generally decreasing with increasing distance from the root, with a suggestion of a region of decreased concentration near 10 cm from the root, where the zinc concentration was increased.

Two hairs from Subject B were then soaked in the radioarsenic solution for 14 h with the results shown in Fig. 2. The results are again strikingly different from those observed for absorption of copper [6] and zinc [7] for hairs taken at the same time from this sub-

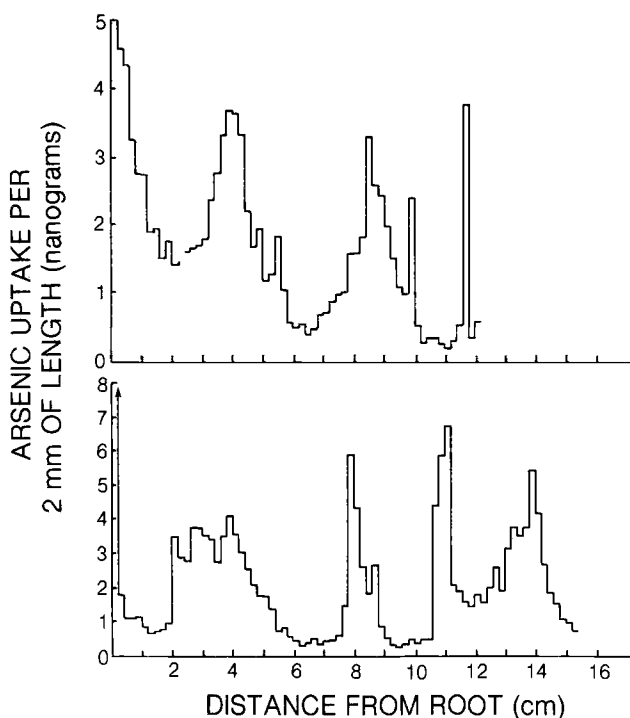


FIG. 2—Arsenic absorption patterns observed in two hairs from Subject B. Soaking time was 14 h.

ject; this time, however, regions of sharply increased concentration are observed periodically down the hair, at almost the same respective distances from the root in the two hairs examined. Had these been measurements of indigenous arsenic content, the data might well have been interpreted in terms of larger than normal ingestion at intervals roughly 4 months apart.

The experiment was repeated with one hair from Subject I and a soaking time of 14 h, with the result shown in Fig. 3. The data indicate that the phenomenon of a sharply peaked absorption pattern is not confined to one subject alone. In this case, however, the peak spacings are not so regular.

The three subjects thus far examined were those for whom highly structured patterns were observed previously for copper and zinc absorption. In view of the absence of correlation observed between patterns for these elements and those now observed for arsenic, it was considered of interest to examine arsenic absorption patterns in hairs of a subject for whom the copper and zinc patterns were flat and featureless. Subject E showed these characteristics, and two of her hairs were soaked next in the radioarsenic solution (for 14 h), with the result shown in Fig. 4. The patterns are certainly featureless, although some decrease in concentration along the first 5 cm from the root is to be noted. Evidently the absence of zones of enhanced copper and zinc absorption was accompanied by an absence of corresponding zones of enhanced arsenic absorption.

In the previous studies [6,7], bleaching of hair was observed to increase sharply the capacity for absorption of copper, zinc, and cobalt. The corresponding situation for arsenic was examined in two hairs from Subject H. The first exhibited a bleached region from 13 cm from the root onwards, and after soaking exhibited the pattern shown in the upper part of Fig. 5. An abrupt *drop* in the concentration of absorbed arsenic in the bleached region is observed, in contrast with behavior for copper, zinc, and cobalt. A

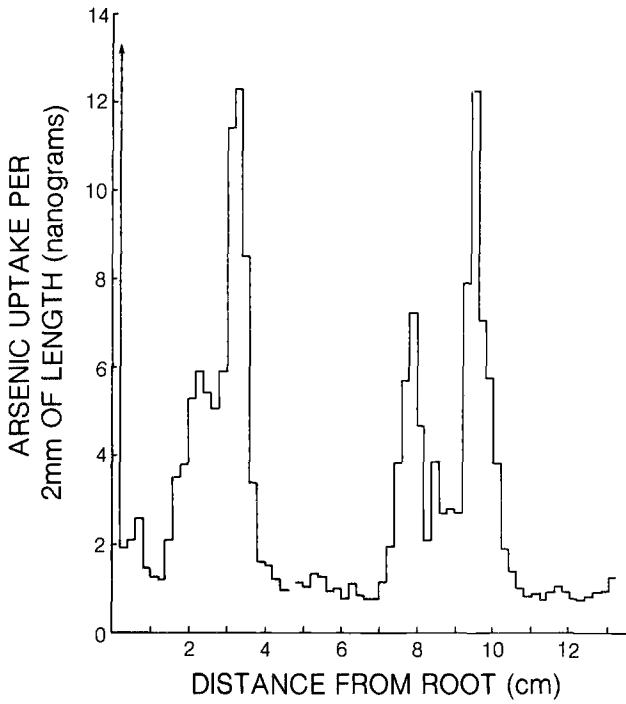


FIG. 3—Arsenic absorption pattern observed in a hair from Subject I. Soaking time was 14 h.

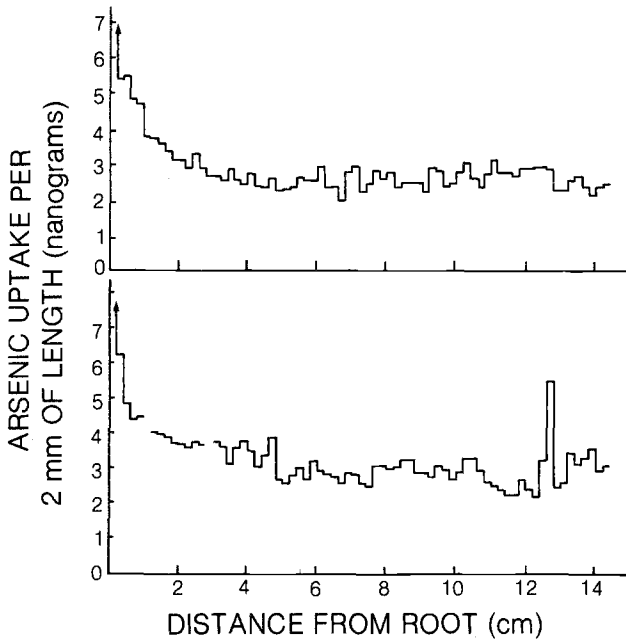


FIG. 4—Arsenic absorption patterns observed in two hairs from Subject E. Soaking time was 14 h.

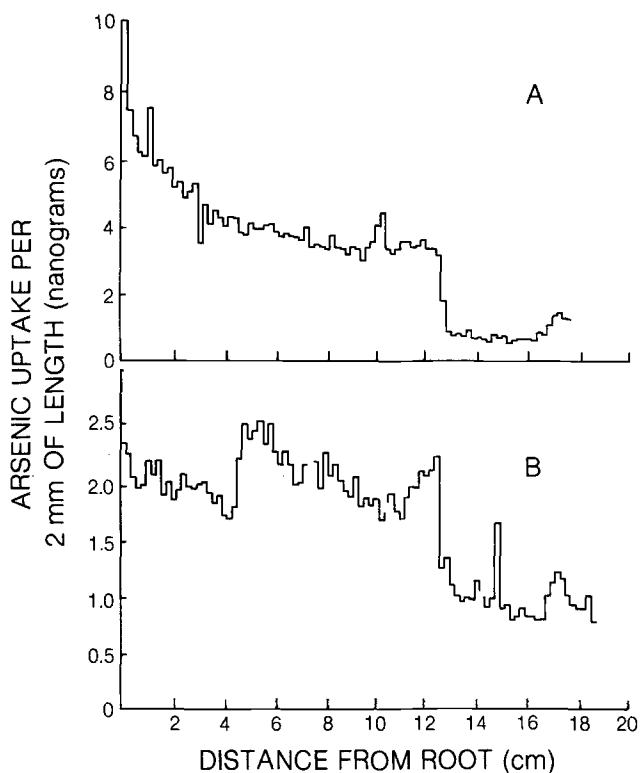


FIG. 5—Arsenic absorption patterns observed in two hairs from Subject H. Soaking time was 14 h. (A) Hair exhibiting a bleached region from 13 cm from the root onwards and (B) hair which had been redyed after bleaching.

second hair was plucked from this same subject, but after the bleached region had been redyed. The absorption pattern for this hair is shown in the lower part of Fig. 5, and still shows a decreased arsenic concentration from about 13 cm from the root onwards, even though a color change there was no longer visible. The decreased concentration in the region between 0 and 4 cm from the root is, however, not explained.

Discussion

The highly structured concentration patterns for absorbed arsenic presented in Figs. 2 and 3 above, when combined with the earlier data of Lima [5], indicate that arsenic ingested at a given time and subsequently excreted in sweat could, at least in some subjects, result in peaks in arsenic concentration at various locations down the existing hair shafts, and not just in the keratin produced in the follicles at that time and later. Thus, interpretation of peaks in arsenic concentration patterns in hairs as indicative of dates of abnormally high arsenic ingestion is a process of uncertain validity.

That is not to say that elevated average arsenic concentrations in hair are not indicative of abnormal arsenic ingestion, provided the hair is known not to have been exposed to significant external contamination (other than sweat). However, structured arsenic patterns can evidently arise both from dietary and nondietary sources (for example, sweat or external contamination).

The data presented here also indicate some chemical specificity in the sites that bind ions in hair, since copper and zinc are evidently bound in greater concentrations in

locations where arsenic is not and vice versa. As far as hair absorption patterns considered as a hair characterization tool are concerned, arsenic patterns combined with those for copper and zinc continue to appear promising. Further work is indicated to determine the extent to which such patterns are characteristic of the individual and to establish methods of measuring this quantitatively.

Summary

Single head hairs from several subjects have been soaked in arsenic radiotracer solution and the arsenic absorbed on 2-mm hair segments has been determined by radioactivity assay. The absorption patterns were characterized for some subjects by regions of high uptake where (in other hairs from the same subject) regions of low uptake of copper and zinc were found, and vice versa. These data have been interpreted in terms of varying densities of binding sites in the hair structure, with specific chemical character.

Arsenic absorption patterns for other subjects were highly structured, showing zones of very high and very low absorption. The dangers of interpreting similar patterns for the indigenous arsenic content of hair in terms of the dates on which elevated arsenic ingestion took place have been discussed.

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References

- [1] Pearson, E. F. and Pounds, C. A., *Journal of the Forensic Science Society*, Vol. 11, No. 4, 1971, pp. 229-234.
- [2] Smith, H., *Journal of the Forensic Science Society*, Vol. 4, No. 4, 1964, pp. 192-199.
- [3] Forshufvud, S., Smith, H., and Wassen, A., *Nature*, Vol. 192, No. 4798, 1961, pp. 103-105.
- [4] Forshufvud, S., Smith, H., and Wassen, A., *Archiv fur Toxikologie*, Vol. 20, 27 May 1964, pp. 210-219.
- [5] Lima, F. W., *Proceedings of the First International Conference on Forensic Activation Analysis*, Gulf General Atomic, Inc., San Diego, Calif. 1967, pp. 261-278.
- [6] Maes, D. and Pate, B. D., *Journal of Forensic Sciences*, Vol. 21, No. 1, 1976, pp. 127-149.
- [7] Maes, D. and Pate, B. D., *Journal of Forensic Sciences*, Vol. 22, No. 1, 1977, pp. 75-88.

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