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# Circadian characteristics of serum calcium, magnesium and eight trace elements and of their metallo-moieties in urine of healthy middle-aged men

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## Abstract

**Objective:** To monitor the around-the-clock distribution of serum and urine concentrations of calcium, magnesium and eight trace elements and of those same elements in urine after their dialysis, and to statistically describe their circadian characteristics by chronobiological procedures.

**Materials and methods:** Serum and urine samples were collected every 3h over a single 24h period from eleven clinically-healthy male subjects, 41-60 years of age, and were analyzed for calcium (Ca), magnesium (Mg), iron (Fe), copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), cobalt (Co), chromium (Cr), and nickel (Ni). Urines were also sequentially dialyzed against ammonium-barbituric acid buffer at pH 7.35 $\pm$ 0.02 using a 12,000-14,000 molecular weight exclusion sieve and then reanalyzed for the same elements. Urine concentrations were adjusted by urine volume to reflect a 3h excretion rate. Time-series were analyzed for circadian time-effect by ANOVA and for rhythm characteristics by the single cosinor fitting procedure.

**Results:** The dialysis effectively removed 90% of total solids, 97% of urea, 92% creatinine, 72% uric acid, and essentially all of glucose. It also removed 99% of potassium (K), 96% of sodium (Na), 65% of Ca and P, 55% of Mg, 41% of Zn and 88% of Ni. A significant or borderline-significant 24h rhythm in serum was detected for Ca, Mg, Fe, Cu, Zn, Cd and Cr; in untreated urine for Ca, Fe, Cu, Zn, Ni, creatinine and volume; and in dialyzed urine for Ca, Fe, Cu, Zn, Pb, Cr, Cd and Ni. A 12h component was significant or borderline-significant in serum for Mg, Fe, Zn, and Cd; in untreated urine for volume, creatinine, Ca, Mg, Cu, and Ni; and in dialyzed urine for Ca, Mg, Fe, Cu, Zn, and Cr. In general, values in serum were lowest near the onset of sleep and highest in the first half of the day (between 02:28 and 13:56 h), while highest values in untreated or dialyzed urine were found several hours later in the day and at night.

**Conclusions:** Significant circadian variations were found in levels of nearly every element that was measured in blood and urine of 11 healthy men, but with highest and lowest levels occurring at different times. This suggests not only that urine concentrations need to be adjusted for collection time interval and urine volume, but that different biological limits at different times of the 24h day should be applied for serum and urinary monitoring of trace elements. We also found that the non-dialyzable segments of these elements in urine represent metallo-moieties composed of proteinacious matter greater than 12,000-14,000 Daltons. Further studies would be of interest to reveal time specificity for metabolic functions associated with any of these trace elements.

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