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Relationship Between Trace Metal Concentrations and Hardness in Drinking Water in Taiwan

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The relationship between water hardness and mortality from cardiovascular disease has been studied for more than thirty years. The association was first described in Japan (Kobayashi 1957) where a significant negative correlation between drinking water hardness and mortality from cerebrovascular disease was found. Subsequently, a number of studies conducted in various countries have demonstrated a negative association between cardiovascular mortality and water hardness (Biorck et al. 1965, Leoni et al. 1985, Morin et al. 1985, Morris et al. 1961, Neri and Johansen 1978, Pocock et al. 1981, Rylander et al. 1991, Schroeder 1960, Yang et al. 1996).

The hardness of drinking water is determined largely by its content of calcium and magnesium. It is expressed as the equivalent amount of calcium carbonate that could be formed from the calcium and magnesium in solution. Two theories have been offered concerning the causative agent responsible for the relationship between death rates from cardiovascular disease and water hardness. One is that soft water is more corrosive than hard water, and thus promotes the dissolution of cadmium, lead and other toxic substances from the plumbing system into the drinking water (Westendorf and Middleton 1979). Another theory is that there is a protective effect from magnesium in water (Karppanen 1986, Marier 1986, Itokawa and Durlach 1989) which was tested in our previous study (Yang 1998).

This study was designed to test the former hypothesis, i.e., to examine whether soft water contains more lead, cadmium, and other metals than hard water.

MATERIALS AND METHODS

Taiwan is divided into 361 administrative (geopolitical) districts, which are referred to here as municipalities (cities or townships) and were used as the sampling units for this study. Excluded from the sampling were 30 aboriginal townships and 9 islets. This elimination of unsuitable municipalities yielded 322 municipalities. Thirty-four municipalities were randomly selected from the 322 municipalities as our study areas. The Tseung (village) are the basic administrative units within each municipality in Taiwan. Five tseungs were randomly selected from each of the 34 municipalities. This study population included 170 tseungs.

In each tseung, one water sample was collected from one household tap water. The household was selected at random and in all 170 water samples were collected. The samples were collected in the period from April to July of 1998. Polythene bottles (1,000 ml) were cleaned using a modified procedure of Laxen and Harrison (1981): the bottles were first soaked in 10% HNO_3 for 48 hours, then in deionized water for a few minutes, and finally rinsed three times with water from a Milli-Q purification unit (Millipore Corp., U.S.A.). Before sampling, water was run through the taps for at least 5 minutes and 0.5 ml HNO_3 was added immediately after collection of a water sample. A Hitachi Z-6100 atomic absorption spectrometer was used to determine the concentration of trace metals (Pb, Cd, Cu, Cr, Zn) in the drinking water. For the analysis of total hardness analysis, an EDTA titrimetric method was used (APHA 1985).

For the comparison of the mean concentrations of trace metals among different hardness levels, analysis of variance (ANOVA) was performed. If a significant result was found, the Tukey multiple comparison test was used to compare all pairs of hardness groups (Kleinbaum et al. 1988). Data analyses were performed using the Statistical Analysis System (SAS) for personal Computers (SAS 1989).

RESULTS AND DISCUSSION

Summary statistics for all analytical results (Table 1) show that there are large variations in the concentration of trace metals and hardness in drinking water in Taiwan.

Table 1. Concentrations of 5 trace metals and hardness levels (mg/L) in tap water of 170 households.

Constituent	Detection limit	Median	mean± SD [a]	Range
Hardness	NA [b]	132.0	128.49±54.28	32-344
Lead	0.010	0.015	0.025±0.014	ND-0.092
Cadmium	0.002	ND [c]	0.003±0.001	ND-0.007
Zinc	0.003	0.008	0.036±0.091	ND-0.570
Copper	0.005	ND	0.021±0.043	ND-0.310
Chromium	0.003	0.007	0.015±0.011	ND-0.056

[a] Mean of detectable observations± standard deviation
[b] Data not available
[c] Not detectable

Generally water with less than 75 mg/l of $CaCO_3$ was classified as soft water, 75-150 mg/l was moderately hard, and above 150 mg/l as hard (Sawyer and McCarty 1978). Table 2 shows the mean concentrations of trace metals according to water hardness. Soft water, moderately hard water, and hard water showed no significant differences in their copper and chromium concentrations, Soft water tends to have higher levels of lead. However, hard water showed higher zinc concentration than that of soft and moderately hard water.

The possible association between a low level of lead exposure and hypertension/cardiovascular disease has been treated in depth in four reviews (Sharp et al. 1987, Pocock et al. 1988, Wojtczak-garoszowa and Kubow 1989, Moller and Kristensen 1992). The hypothesis that soft water is harmful because of lead corrosion has been a subject of investigation for more than 30 years, However, the results are inconclusive. Some show plumbosolvency in hard water as well as soft water (Crawford and Morris 1967, Crawford and Clayton 1973) another showed plumbosolvency only in soft water (Neri et al. 1975). Anderson et al. (1975) however, found lead levels slightly higher in hard water. Our study is consistent with Neri et al. (1975) and found that lead levels were significantly higher in soft water than in moderately hard or hard water. The determinants of lead levels in tap water are apparently complex (Sharrett 1979).

Table 2. Concentration of trace metals (mg/L) in household tap water stratified by hardness levels

Trace metal	Soft water [a] mean±SD [d] (n=23)	Moderate hard [b] mean±SD (n=114)	Hard water [c] mean±SD (n=33)	ANOVA test
Lead	0.040±0.024 *[f] (ND-0.092) [e]	0.023±0.010 (ND-0.054)	0.021±0.008 (ND-0.047)	p=0.0001
Cadmium	0.004±0.002 *[f] (ND-0.007)	0.003±0.001 (ND-0.005)	0.003±0.001 (ND-0.004)	p=0.004
Zinc	0.030±0.042 *[f] (ND-0.140)	0.015±0.018 *[f] (ND-0.093)	0.099±0.176 (ND-0.570)	p=0.0001
Copper	0.010±0.004 (ND-0.140)	0.013±0.015 (ND-0.080)	0.035±0.066 (ND-0.310)	p=0.1769
Chromium	0.024±0.028 (ND-0.056)	0.015±0.010 (ND-0.041)	0.015±0.009 (ND-0.039)	p=0.3786

[a] Total hardness: 0-75 mg/L as $CaCO_3$.

[b] Total hardness: 75-150 mg/L as $CaCO_3$.

[c] Total hardness: over 150 mg/L as $CaCO_3$.

[d] Mean of detectable observations± standard deviation

[e] Values in parentheses indicate the range

[f] Values within a row with asterisks were found to be significantly different from unmarked values using Tukey's multiple comparison

Schroeder and Kraemer (1974) showed that corrosiveness of municipal drinking water was associated with elevated cardiovascular death rates and speculated that cadmium corroded from galvanized water pipes may be the water factor in cardiovascular diseases. However, data from previous studies were inconsistent. Some found that cadmium levels were higher in hard water (Anderson et al. 1975, Masironi 1970). Crawford et al. (1968) found no association between cadmium and hardness. Our study found cadmium levels are higher in soft water. Cadmium levels in drinking water appear not to be closely associated with water hardness. It may be because corrosion is not determined primarily by water hardness, or because cadmium levels in drinking water are not determined primarily by corrosion (Sharrett 1979).

The relationship between zinc levels in tap water and hardness has not been reported consistently. Anderson et al. (1975) reported a negative association between zinc and hardness. Some studies found zinc to be unrelated to hardness (Crawford and Morris 1967, Punsar et al. 1975). Our study found a positive correlation between zinc levels and hardness and is consistent with some previous studies (Masironi 1970, Neri et al. 1975, Elwood et al. 1974).
The association between chromium levels in drinking water and hardness was also inconsistent. Chromium levels were noted to be significantly higher in hard water than in soft water (Masironi 1970, Neri et al. 1975, Punsar et al. 1975, Voors 1971). While other reports showed no association between chromium and hardness (Schroeder 1966, Neri et al. 1975, Anderson et al. 1975, Crawford and Morris 1967, Elwood et al. 1974). Our study found chromium concentrations did not differ markedly between water hardness groups.

Copper levels were found to have a positive correlation with hardness (Masironi 1970, Neri et al. 1975, Crawford and Morris 1967, Elwood et al. 1974). While other reports showed a negative association between copper and hardness (Schroeder 1966, Neri et al. 1975, Anderson et al. 1975). Our study found copper concentrations did not significantly differ among the three hardness groups.

In conclusion, the relationship between the 5 trace metals studied and hardness levels had little consistency with reports from other studies, indicating a weakness inherent in geographic studies of this type. Since soft water has higher levels of lead, the possibility that our previously reported negative association between coronary mortality and hardness levels may be, at least partially, due to the high concentration of lead in soft water and this may be a casual relationship.

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