

## Trace Elements in Ground Water of Metro Cebu, Philippines

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### Abstract

Contaminants in drinking water present public health risks. Concentrations of some elements (Ca, Cd, Co, Cu, Fe, Pb, Li, Mg, Mn, Ni, Pd, K, Na and Zn) in drinking water were measured in ground waters from deep wells and pumping stations of Metro Cebu, Philippines. The analysis performed by atomic absorption spectroscopy, indicated that mostly the elements were below the WHO or EEC guidelines; except for chromium. The presence of the elements is indicative of the lithologic composition of the region, which is mainly of limestone formations, rather than of anthropogenic sources.

**Key words:** Cebu Philippines, elements, ground water

### Introduction

Metro Cebu is highly dependent on ground water as a source of drinking water, for agriculture, for industry and in some cases as a source for surface water habitats. Nearly all human activities have the potential to adversely affect Cebu's ground water quality and quantity. In addition, the region's population is expected to grow, with most of the growth directed toward the coastal areas where water resources are already threatened by over-consumption, contamination, and salt-water intrusion. The complexity of Cebu's ground water resources and the high cost of monitoring may prevent the development of a complete picture of the nature and extent of the region's ground water problems. The Metro Cebu Water District (MCWD) is responsible for the management and distribution of water supply. MCWD conducts regular bacteriological test but limited physico-chemical analysis on water. Despite the amount of work done in other countries, there had been no published studies on metals in drinking water in Metro Cebu. For this reason, ground water samples were collected from different groundwater sources to ascertain the water quality (element content) for domestic consumption using WHO guidelines. In the absence of guideline values for some metals, the EEC criteria is used.

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## Materials and Methods

### Water samples

Ninety (90) ground water samples were collected from MCWD wells and pumping stations situated in Compostela, Lilo-an, Consolacion, Mandaue City, Cebu City, Talisay and, Mactan Island of Metro Cebu, Philippines (Fig. 1) from June to August 2004. Water samples were placed in polyethylene bottles, which were previously acid-washed and rinsed with portions of distilled water and water sample. The water samples were filtered immediately using  $0.45\ \mu\text{m}$  filter paper and filtrates acidified to pH 2 in order to keep the metals in solution. All samples were stored in a dark and cool environment,  $4^{\circ}\text{C}$ .

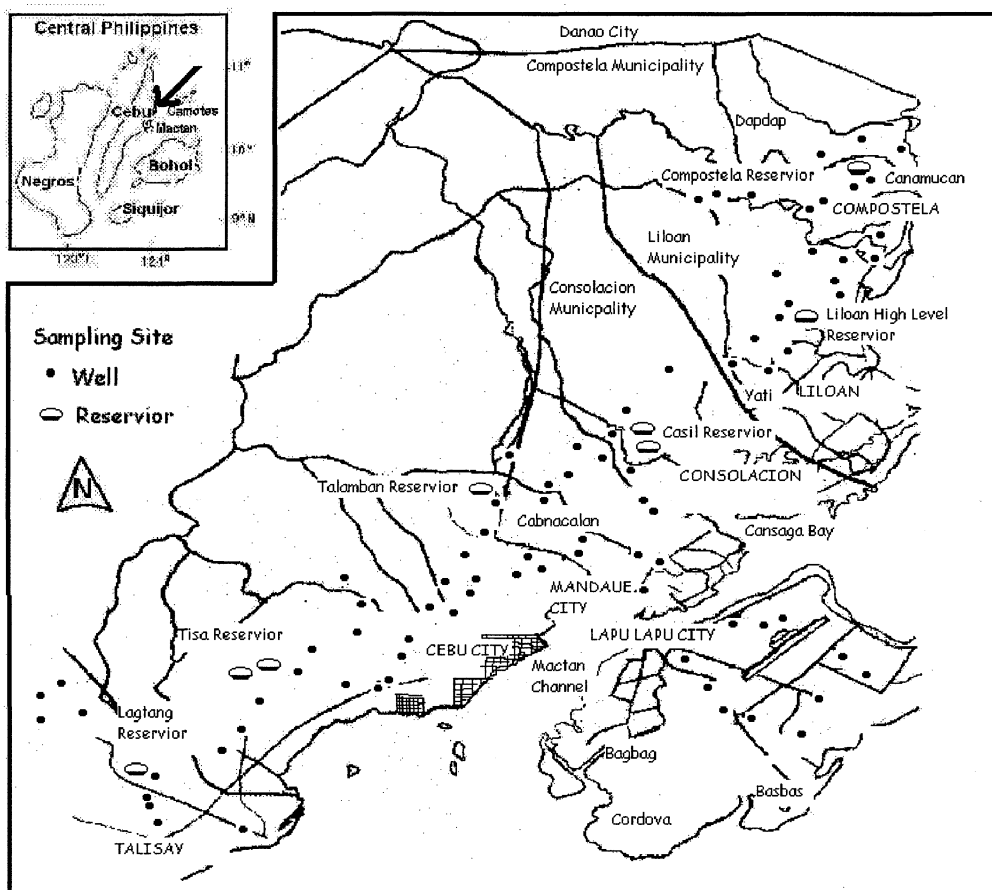


Fig. 1. A map of Metro Cebu, Philippines showing the sampling sites used in the study.

### Measurement and analysis

The metal analysis was performed according to standard method (APHA, 1992), and using atomic absorption spectroscopy (Shimadzu AA-6200 spectrophotometer). All solutions were prepared with deionized water. Stock solutions of all metals, containing 1000 ppm were used for the preparation of the standards for the calibration curve. The

precision of the measurements was checked by taking three replicates from the sample and including a blank in each batch. Percentage recuperation for all elements was above 97% and the percentage CV below 5%.

## Results and Discussion

There is an increasing worldwide concern about the quality of water. Epidemiological studies have indicated a strong association between the occurrence of several diseases and the presence of metals. Excessive or deficient of essential micronutrients may have detrimental effects on health. The World Health Organization (WHO 1993) and the European Economic Community (EEC 1980) recommended general guidelines for the quality of water used for human consumption. However, it is generally recognized that the dietary intake is the main contributing factor to the uptake of metals by man.

Water in Metro Cebu may come from springs and deep wells. Deep well extract groundwater and are pumped directly to the reservoirs. Then, water is distributed to the consumers through the force of gravity. Data for the total dissolved concentrations of calcium (Ca), cadmium (Cd), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), nickel (Ni), palladium (Pd), potassium (K), sodium (Na) and zinc (Zn) in ground water taken from ninety (90) MCWD deep wells and pumping stations, are shown in Table 1. Water sample from Mactan Rock Spring Source was found to contain high metal concentrations compared to other water sources, due to the brackish characteristic of the water.

The averaged metal and range concentrations obtained from the 90 water samples, together with guideline values are summarized in Table 2. The Cd, Cu, Fe, Mn, Na, Ni, Pb, and Zn are within the WHO or EEC guidelines. Relatively low values of trace elements are found in these samples of ground water under study and indicated that these are far from pollution sources. These values are available under ordinary conditions due to lithologies composition of the region. However, it might be possible that water samples may contain Cd, Fe, Ni, and Pb concentrations exceeding the WHO or EEC guidelines, since the detection limits of respective metals are higher than the WHO or EEC guideline values. In this study, Cd, Fe, Ni, and Pb should be a matter of concern.

Cadmium is a cumulative toxic metal and the kidney is the main target for Cd toxicity. Secondary to kidney damage, the effect of Cd on the bone causing osteoporosis (YOSHIKI *et al.* 1975, ANDERSON *et al.* 1978, LUI *et al.* 1991) has been well documented. Although Fe is essential for man (AGGETT 1985, PLEBAN *et al.* 1985) in excess, accumulation is harmful. The mutagenicity of iron, nephrotoxicity, and induction of renal cell and hepatocellular carcinoma have been well documented (BOYCE *et al.* 1986, WONG 1988, FARGION *et al.* 1991) due to the formation of oxygen free radicals which may be proximate carcinogens (STEVENS, 1990). A case study by PLATSCHEK *et al.* (1989) revealed a brown discoloration of the nail and hair due to washing with water with a high Fe content. A recent study by DUTRA-DE-OLIVEIRA *et al.* (1994) showed that Fe-enriched drinking water could be an alternative way to supply Fe to children. There is a

possibility of leaching processes from water taps and fixtures which could contribute to nickel levels in drinking water (WHO 1991). In relation to pulmonary exposure, Ni is now considered as a human carcinogen (GRANDJEAN *et al.* 1988, SHEN *et al.* 1999). On the other hand, there is a lack of data on carcinogenicity of Ni by the oral route. Recent studies have shown that a low dietary intake of Ni reduced the activity of dermatitis (VEIEN *et al.* 1993, SANTUCCI *et al.* 1988, SANTUCCI *et al.* 1990). Lead is a natural element that is persistent in water and soil. Most of the lead in environmental media is of anthropogenic sources. Lead typically leaches into water from lead pipes and plumbing Table 1. Concentration of elements in 90 ground water samples collected from Metro Cebu, Philippines.

MCWD Water Source	Metal Concentration (ppm)								
	Ca	K	Li	Mg	Mn	Na	Pd	Zn	Cd, Co, Cu, Fe, Ni, Pb
1.1	20.52	1.9	nd	15.96	nd	6.8	nd	nd	nd
1.2	10.44	1.4	nd	13.32	nd	7.5	0.22	nd	nd
1.3	27.72	1.7	0.06	16.14	nd	5.6	nd	nd	nd
1.4	25.92	2.4	nd	18.0	nd	9.4	nd	nd	nd
4.10	9.24	1.8	nd	17.4	nd	17.4	nd	nd	nd
4.12	18.72	1.9	nd	17.28	nd	9.8	nd	nd	nd
4.2	25.86	2.8	nd	9.36	nd	15.2	nd	nd	nd
4.7	21.66	1.7	nd	15.84	nd	15.6	nd	nd	nd
4.8	37.68	1.8	0.06	11.34	nd	5.5	nd	nd	nd
5.1	47.52	1.7	nd	7.8	nd	14.5	nd	nd	nd
5.2	28.14	1.5	nd	6.66	nd	7.4	nd	nd	nd
5.3	30.9	1.1	0.06	3.37	nd	2.2	nd	nd	nd
5.4	25.08	0.8	nd	1.07	nd	nd	nd	nd	nd
5.5	32.46	1.4	0.05	7.56	nd	7.2	nd	nd	nd
5.6	30.12	1.4	nd	4.08	nd	7.8	nd	nd	nd
5.7	35.46	1.3	nd	3.18	nd	2.1	nd	nd	nd
Ayala 1	7.38	2.2	nd	18.9	nd	20.8	nd	nd	nd
Can 2	26.94	2.8	nd	17.04	nd	16.0	nd	nd	nd
Can 3	39.48	2.6	nd	14.52	nd	6.4	nd	nd	nd
Can 5	35.28	2.5	nd	16.68	nd	6.9	nd	nd	nd
Cebu Plaza	23.82	1.7	nd	15.66	nd	17.6	nd	nd	nd
G-1	20.76	1.0	nd	12.12	nd	9.2	nd	nd	nd
G-2	9.66	2.2	nd	18.72	0.07	6.4	nd	nd	nd
G-3	26.1	2.3	nd	18.0	nd	18.8	nd	nd	nd
G-5B	25.66	2.4	nd	16.56	nd	6.8	nd	nd	nd
G-7	19.5	2.1	nd	17.76	nd	13.9	nd	nd	nd
G-9	12.66	0.9	nd	7.8	nd	9.8	nd	nd	nd
K2.2	33.78	1.4	nd	6.7	nd	9.0	nd	nd	nd
K2.4	49.92	3.0	nd	2.7	nd	18.2	nd	nd	nd
K3.1	10.14	3.2	nd	17.9	nd	12.7	nd	nd	nd

Con't of Table 1.

MCWD Water Source	Metal Concentration (ppm)								
	Ca	K	Li	Mg	Mn	Na	Pd	Zn	Cd, Co, Cu, Fe, Ni, Pb
L-1	8.46	1.7	nd	12.7	nd	14.4	nd	nd	nd
L-2	41.7	2.5	nd	15.4	nd	7.5	nd	nd	nd
L-3	17.18	2.1	nd	15.5	nd	21.3	nd	nd	nd
L-4	1.01	1.5	nd	13.0	nd	10.7	nd	nd	nd
L-5	18.84	1.4	nd	10.6	nd	7.1	nd	nd	nd
L-7	14.84	2.1	nd	16.3	nd	13.3	nd	nd	nd
Mac1	48.66	4.7	nd	13.6	nd	26.7	nd	nd	nd
Mac3	43.2	3.5	nd	9.4	nd	35.1	nd	nd	nd
Mac4	35.76	3.6	nd	6.4	nd	16.2	nd	nd	nd
Mg1	26.76	1.3	nd	13.7	nd	7.0	nd	nd	nd
Mg2	27.3	1.6	nd	14.2	nd	6.7	nd	nd	nd
Mg6	22.2	1.4	nd	13.6	nd	7.6	0.24	nd	nd
Mg10	38.56	1.9	nd	16.0	nd	5.3	nd	nd	nd
Mg14	34.98	2.1	0.06	16.9	nd	7.2	nd	nd	nd
Mg16	26.22	2.1	nd	17.4	nd	17.0	nd	nd	nd
Mg18	29.7	1.5	nd	14.8	nd	10.8	nd	nd	nd
Mg19	27.6	1.7	nd	16.0	nd	6.6	nd	nd	nd
P-2	18.6	2.3	nd	19.1	nd	14.9	nd	nd	nd
P-4	15.78	2.8	nd	19.0	nd	14.6	nd	0.20	nd
P-6	20.46	1.9	nd	18.5	nd	10.2	nd	nd	nd
SV1	40.74	1.8	nd	5.1	nd	6.8	nd	nd	nd
SV2	51.12	3.0	0.06	10.4	nd	15.5	nd	nd	nd
SV3	47.1	2.3	nd	4.7	nd	16.6	nd	nd	nd
SV4	43.56	1.3	nd	0.59	nd	8.4	nd	nd	nd
SV5	49.14	2.3	nd	8.28	nd	26.3	nd	nd	nd
SV6	46.5	1.1	nd	-	nd	12.5	nd	nd	nd
SV8	48.12	1.5	0.06	3.5	nd	12.6	nd	nd	nd
SV9	55.62	2.3	0.11	8.8	nd	27.6	nd	nd	nd
SV10	70.56	3.8	nd	14.9	nd	45.6	nd	nd	nd
SV11	56.1	2.8	nd	10.3	nd	17.3	nd	nd	nd
SV12	60.3	2.3	nd	9.9	nd	16.0	nd	nd	nd
SV13	48.48	2.8	nd	11.2	nd	40.3	nd	nd	nd
SV14	57.66	1.5	nd	1.92	0.07	16.5	0.45	nd	nd
SV15	54.0	3.9	nd	17.2	nd	29.1	nd	nd	nd
SV17	32.64	1.6	nd	7.3	nd	20.3	nd	nd	nd
T-5	31.56	3.4	nd	18.1	nd	14.0	nd	nd	nd
W-2	31.98	2.1	nd	17.6	nd	9.6	nd	nd	nd
W-3.2	40.38	1.8	nd	6.9	nd	9.7	nd	nd	nd

Con't of Table 1.

MCWD Water Source	Metal Concentration (ppm)								
	Ca	K	Li	Mg	Mn	Na	Pd	Zn	Cd, Co, Cu, Fe, Ni, Pb
W-3.3	43.44	2.5	nd	12.0	nd	5.8	nd	nd	nd
W-4	13.68	3.7	nd	18.1	nd	17.6	nd	nd	nd
W-9	22.56	1.7	nd	14.5	nd	8.0	nd	nd	nd
W-11	26.28	2.1	nd	15.3	nd	19.0	nd	nd	nd
W-12	22.98	2.6	nd	18.3	nd	11.4	nd	nd	nd
W-13	22.2	2.4	nd	18.5	nd	9.6	nd	nd	nd
W-13B	27.36	3.1	0.06	18.42	nd	11.4	nd	nd	nd
W-15	20.94	1.9	nd	14.78	nd	7.3	nd	nd	nd
W-17	10.14	1.2	nd	7.56	nd	4.4	nd	nd	nd
W-18	20.58	2.3	nd	15.06	nd	13.6	nd	nd	nd
W-25	11.04	2.3	nd	17.82	nd	10.9	nd	nd	nd
W-29	13.74	2.3	0.06	10.44	nd	6.9	nd	nd	nd
W-30	6.84	1.8	nd	11.88	nd	11.5	nd	nd	nd
W-31	3.6	1.7	nd	13.26	nd	16.1	nd	nd	nd
W-49	9.0	0.8	nd	13.5	nd	6.5	nd	nd	nd
*1)	31.56	2.0	nd	15.78	nd	9.8	0.23	nd	nd
*2)	28.28	2.7	nd	18.84	nd	21.4	nd	nd	nd
*3)	28.44	2.4	nd	15.36	nd	7.7	nd	0.04	nd
*4)	45.0	2.1	nd	11.94	nd	14.8	nd	nd	nd
*5)	29.1	1.6	nd	16.8	nd	10.4	nd	nd	nd
*6)	41.88	1.8	nd	16.9	nd	14.3	nd	nd	nd
*7)	20.58	1.4	nd	14.4	nd	3.7	nd	nd	nd
*8)	3.66	2.7	0.06	19.3	nd	10.5	nd	nd	nd
*9)	82.44	8.2	0.06	19.9	nd	95.2	0.26	nd	nd
*1) Tisa (Fin) Filter	31.56			*4) Tisa Buhisan Spring Source				*7) SVL - Abejo	
*2) Tisa (Raw) Filter	28.28			*5) Well 2 - Abejo				*8) Formost, Linao, Minglanilla	
*3) Tisa Buhisan Dam				*6) Well 3 - Abejo				*9) Mactan Rock Spring Source	
nd - none detectable				- not analyzed					

fittings. The systemic toxic effects of lead in humans have been well-documented by the EPA (1989) and ATSDR (1993) and showed that lead is a multi-targeted toxicant, causing effects in the gastrointestinal tract, hematopoietic system, cardiovascular system, central and peripheral nervous systems, kidneys, immune system, and reproductive system.

Many metals are unstable in the presence of water and have a tendency to transform or degrade to more stable and often soluble forms by "corrosion". This process is characterized by partial solubilization of the materials constituting the treatment and supply systems, tanks, pipes, valves and pumps. The rate at which corrosion takes place is governed by many chemical and physiological factors. High concentrations of Cd, Fe, Cu and Zn can be attributed to the corrosive nature of the water in the distribution pipes

and water tanks. It could be expected that distribution pipes, and storage tanks may be a source of contamination if not properly installed and maintained.

Table 2. Summary of metal concentration of water samples collected from Metro Cebu, Philippines, together with guideline values..

Element	Mean $\pm$ S.D.* (ppm)	Range (ppm)	WHO Guideline Limit(ppm)	Detection Limit(ppm)
Ca	29.66 $\pm$ 15.65	1.01-82.44	-	0.33
Cd	-	-	0.003	0.01
Co	-	-	-	0.17
Cu	-	-	2	0.008
Fe	-	-	0.05**	0.21
K	2.16 $\pm$ 0.97	0.8-8.20	-	0.12
Li	0.06 $\pm$ 0.01	nd-0.11	-	0.05
Mg	13.04 $\pm$ 5.04	0.59-19.92	-	-
Mn	0.06 $\pm$ 0.0007	nd-0.07	0.5	0.06
Na	13.84 $\pm$ 11.53	nd-95.20	200	1.61
Ni	-	-	0.02	0.23
Pb	-	-	0.01	0.18
Pd	0.28 $\pm$ 0.09	nd-0.45	-	0.22
Zn	0.12 $\pm$ 0.12	nd -0.20	3	0.01

\*none detectable or below detection limit values were excluded in the calculation nd - none detectable  
\*\*EEC guideline value

Ca, Co, K, Li, Mg and Pd were also detected in all the water samples tested. No health-based guidelines were proposed for these elements. The main cations order are Ca > Na > Mg > K. This order is due to the lithologic composition of the region, which is mainly of limestone formations. The weathering of minerals (Ca and Mg) may also increase the amount of ions in water. Calcium is sometimes referred to as lime. It is an essential component for the preservation of the human skeleton and teeth. It also assists the functions of nerves and muscles. The use of more than 2.5 grams of calcium per day without a medical necessity can lead to the development of kidney stones and sclerosis of kidneys and blood vessels. Generally non-toxic, but extremely high doses can cause kidney stones. (PAK *et al.* 1987, BATAILLE *et al.* 1983) and increase the risk of prostate cancer (GIOVANNUCCI *et al.* 1998). High-calcium diets may have a deleterious effect upon bone mineralization because of their hypomagnesian (magnesium-depleting) effect (RUDE *et al.* 1976) and can interfere with the absorption of phosphorus, which, like calcium, is important for bone health (HEANEY *et al.* 2002). Cobalt is an essential element which enters the body in vitamin B12 (KORC 1988). Excessive exposure to Co may occur in industrial situations and a recent study by LAUWERYS and LISON (1994) revealed that the skin and respiratory tract are the two main target organs. No information is available on the level of Co in water. Since Co is not a cumulative toxin, it was thought that Co levels found in the water samples tested did not represent a health hazard. Potassium

is an essential dietary mineral that is also known as an electrolyte. However, higher exposures of potassium can lead to disturbing heartbeats and irritation of the eyes, nose, throat, lungs with sneezing, coughing and sore throat and hypokalemia (FNB 2004, MANDA 1997). Lithium does not occur in nature in its free form but is found in minerals such as spodumene, petalite, and eucryptite (BELILES 1994). Lithium compounds are found in natural waters and in some foods. The average dietary intake is estimated to be about 2 mg per day (BELILES 1994). Case histories described by GOSSELIN *et al.* (1984) indicate that doses of 12-60 g (171-857 mg/kg/day for a 70 kg person) can result in coma, respiratory and cardiac complications, and death in humans. Adverse effects have not been identified from magnesium occurring naturally in food. However, adverse effects from excess magnesium intakes have been observed. Symptom of excess magnesium supplementation is diarrhea, fall in blood pressure (hypotension), lethargy, confusion, disturbances in normal cardiac rhythm, and deterioration of kidney function (SHILS 1999, FNB 1997). The intake of palladium from food or drinking-water is low. For drinking water, a maximum daily intake of 0.03  $\mu\text{g}$  palladium/person per day has been calculated (assuming a consumption of 2 litres/day). Several palladium and its compounds are of very low to moderate acute toxicity if swallowed (depending mainly on their solubility). Palladium ions have been shown to be potent skin and respiratory sensitizers, causing skin and eye irritation and the immune system is an important target, too (WHO 2002).

In conclusion, low levels of metals were found in this study, and do not represent a particular concern. The conducted study is a preliminary survey. Further studies using sophisticated instrumentation to determine the precise level of toxic element contamination like chromium, mercury and arsenic; as well its impact on the health of the consumers, are recommended. Extensive monitoring is needed in order to establish a background water quality data.

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