# HEAVY METALS IN SEA SALT, SEAWATER SOURCE AND IODIZED SALT LOCALLY FOUND IN ILOILO, PHILIPPINES

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## ABSTRACT

Eating food contaminated with heavy metals could lead to poisoning, long term health problem and even death. One common substance needed for food preparation is salt. Salt can be mined as rock salt or harvested in the sea by evaporating the sea water. Salt can contain heavy metals. This study aimed to determine quantitatively the cadmium, manganese, lead and copper content of sea salt, sea water source and iodized salt. The sea salt and sea water samples were taken from four locations in Iloilo which have salt industry. Iodized salt samples were purchased locally from different grocery stores located in the city of Iloilo. The cadmium content was beyond the allowable limits in both sea salt, sea water source and iodized salt set by DENR, CODEX and WHO. Manganese in sea salt exceeded the allowable limits. Lead exceeded the allowable levels in sea salt and some in sea water source while lead was not detected in iodized salt. Copper was above the allowable limits in sea water source and only on Site C sea salt sample while the iodized salt did not exceed the limits for copper set by DENR, CODEX and WHO.

# INTRODUCTION

*Background and Rationale*

Heavy metals are metallic chemical elements that has a relatively high density range of 3.5 g/cm 3 to above 7g/cm 3 and is toxic at low concentrations (Duffus J.H., 2002). They are dangerous because they tend to bio-accumulate in various organsin biological organism over time. Heavy metals which may lead to health threats are lead (Pb), cadmium (Cd), copper (Cu) and manganese (Mn).Contaminated food and drinks are the major exposure path of heavy metals in most people (Zukowska & Biziuk, 2008).

Salt is a food additive that is commonly used to enhance taste, have countless uses as food preservative and is also used in industries and in medical field. Salt is an ionic white crystalline compound with a chemical formula of NaCl, a molar mass of 58.443 g/mole, melting point of $800.7^{0}C$ and a boiling point of $1,465^{0}C$ (Lide, 2009).

Sea salt is produced by evaporating seawater, leaving behind trace minerals and elements which affect the flavor, color, and texture of the salt obtained. Iodized salt from rock salts is commonly mined from underground salt deposits. The deposits are washed with water to dissolve the salt, forming a salt solution which is then evaporated to form crystals. Table salt added with iodine is called iodized salt (Venkatsh Manner & Dunn, 1995).

National and international agencies set limits on the safe and allowable contents for heavy metals in food and sea water. The Philippine's Department of Environment and Natural Resources (DENR) is the lead agency that monitors and regulates the heavy metal contents of sea water. The World Health Organization (WHO) is an international organization which sets the standards for food safety.

CODEX Alimentarius Commission is an international commission established by the United Nations Food and Agriculture Organization (FAO). It sets the allowable limits for heavy metals in different food stuff.

Lead can cause many health consequences if it enters our body. Inside the body, it accumulates in the bones and teeth which affect the different organs and systems such as central and peripheral nervous systems, gastrointestinal tract, kidney and brain. Ukwo and Edima-Nyah (2016) analyzed sample of iodized salts and reported that lead is present at a range of 0.11-4.21 mg/kg. The maximum level of lead in food grade salt permitted by CODEX is 2.0 mg/kg.

Exposure to cadmium causes bone damage, osteoporosis, and renal tubular dysfunction which eventually can lead to renal failure (Engstrom, et. al., 2012; AL-Rmalli, Jenkins, & Haris, 2012).In the study of Nwochoko, et. al., (2012) on cadmium content of some refined salts in southeastern Nigeria, the value was reported to be 0.02 mg/kg. Whereas Ukwo and Edima-Nyah (2016) reported a concentration 0.34-0.52 mg/kg of cadmium in local iodized salt samples. The maximum concentration of cadmium exceeds the permitted level of cadmium on food grade salt set by CODEX which should only be 0.5 mg/kg (CODEX Stan 2006).

Oral exposure to manganese can result to significant health effects such as neurological problems. Early signs of manganese toxicity include headaches, muscle cramps, fatigue, and aggressiveness which can then lead to Parkinson's disease-like symptoms such as tremors (Aschner, et. al., 2009). The World Health Organization International Standards for Drinking Water determined that 0.5 mg/liter is the allowable limit of manganese.

The World Health Organization (2003) stressed that a level of 2 mg/liter for copper will be the allowable level of copper for foods. Copper can irritate the nose, mouth, and eyes. It can cause diarrhea, dizziness, nausea, cramps and headache. High intakes of copper can cause liver and kidney damage and even death.

*Significance of the Study*

The significance of this study is that those who use salt for different purposes maybe aware of the risk involve in using too much salt.

*Objectives*

This study determined the concentration of Cd, Pb, Cu and Mn in sea salt, sea water source and iodized salt and compare the levels of heavy metals found in these samples with the allowable limits set by WHO, DENR and CODEX.

*Hypothesis*

1. There is no significant difference in the amount of heavy metals in sea salt from the four sites in Iloilo.
2. Sea salt samples passed the limits for heavy metals contents set by CODEX and WHO.
3. Iodized salt samples passed the limits for heavy metal contents set by CODEX and WHO.

*Scope and Limitation*

This study measured the concentrations of Cd, Mn, Pb and Cu in sea salt, sea water source and iodized salt. Sea salt and sea water samples were taken locally from the salt production sites. Iodized salt samples were purchased from different grocery stores located within Iloilo City. The concentration of heavy metals were measured using Agilent

Technologies Atomic Absorption Spectrometer Model 55B. This study did not include the determination of physical properties of sea salt, seawater and iodized salt.

## MATERIALS AND METHODS

*Collection of Samples*

The sea salt and sea water samples were taken from different sea salt production sites in Iloilo as shown in Figure 1.

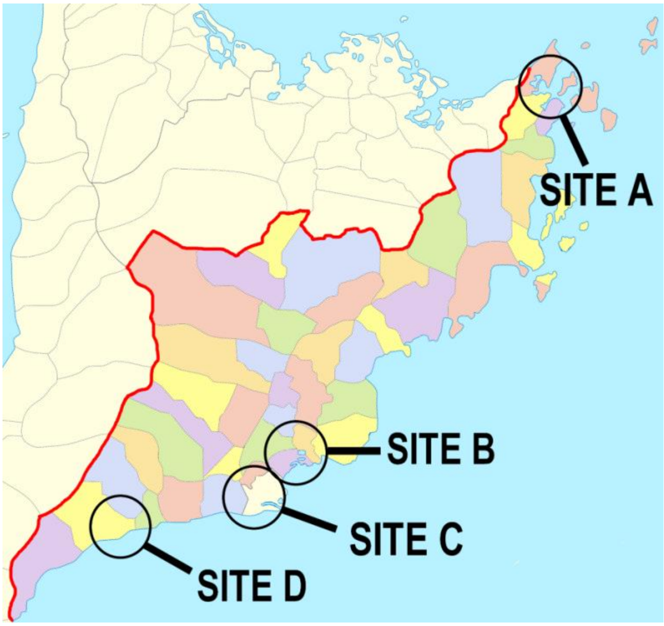


Figure 1. Iloilo Map where sea salt and sea water source samples were collected

Sampling was done between the months of April and May 2017. Three kg of sea salt were obtained from random salt beds, 3L of sea water were taken from production site and 500 gram triplicate iodized salt samples from eight different brands of iodized salt were purchased from different grocery stores in Iloilo City for sampling.

*Preparation of the Sample/Digestion Procedure*

One gram of homogenized and quartered salt samples were placed on acid-washed 250ml beaker and dissolved with 100ml of distilled water. Five ml of concentrated nitric acid and 15ml of concentrated hydrochloric acid were added. The beakers were placed in a hot plate, heated and concentrated to about 50ml. The beakers were cooled and samples were filtered. The filtrates were collected in an acid-washed 100mlvolumetric flask and then made up to 100ml with distilled water (AOAC, 1990).

One hundred milliliters aliquot sea water sample were placed in an acid-washed250ml beaker. Five ml of concentrated nitric acid and 15ml of concentrated hydrochloric acid were added. The beakers were placed in a hot plate, heated and concentrated to about 50ml. The beakers were cooled at room temperature and were filtered. The filtrates were collected in an acid-washed 100mlvolumetric flask and then made up to 100ml with distilled water.

*Instrumentation*

The Atomic Absorption Spectrometer assessed the concentration of analyte in the sample. It requires standards with known analyte content to establish the relation between the measured absorbance and the known concentration.

*Preparation of Standard Solutions*

From the stock 1000 ppm metal solution an aliquot of 10 ml were transferred to 100 ml volumetric flask. The volumetric flask was diluted to mark with distilled water and this constitute 100 ppm of metal which was used for the preparation of calibration curve. For cadmium and manganese, an aliquot of 0.25, 0.5, 1.0, 1.5 and 2.0ml was pipetted from the 100ppm Cd and Mn solutions and was diluted to mark on a 100ml volumetric flask with distilled water. This constitutes the concentrations of 0.25, 0.5, 1.0, 1.5 and 2.0ppm Cd and Mn respectively. For lead calibration, an aliquot of 0.5, 1.0, 1.5, 2.0 and 2.5ml was pipetted from the 100ppm Pb solution and was diluted to mark on a 100ml volumetric flask with distilled water. This constitutes the concentrations of 0.5, 1.0, 1.5, 2.0 and 2.5ppm Pb respectively. An aliquot of 1.0, 2.0, 3.0, 4.0 and 5.0ml was pipetted from a stock 100ppm Cu solution and transferred to a 100ml volumetric flask and diluted with distilled water. This solution constitutes1.0, 2.0, 3.0, 4.0 and 5.0ppm Cu respectively.

*Analysis of Metals Using AAS*

The standard solutions were aspirated to the instrument according to increasing order of concentration and gave absorbance result. Plotting the prepared concentration with its corresponding absorbance would produce a straight line which follow the line equation: $y=mx+b$ (y is the absorbance given by the instrument, m is the slope of the line, b is the line intercept and x is the unknown concentration). Determining the concentration of the unknown would have: $x=(y-b)/m$. Once a standard curve was established, the blank and the sample were aspirated.

*Data Processing and Analysis*

Data were analyzed by One-Way ANOVA and Duncan Multi Range Test (DMRT) using SPSS 17 for significant differences, mean and standard deviations. The data were analyzed at 95% confidence level.

## RESULTS AND DISCUSSION

The comparison of heavy metals in sea salt from different locations in Iloilo is shown in Table 1. Results showed that Cd and Mn levels in all locations exceeded the allowable limit by both CODEX and WHO. Sea salt from all sites passed the limits set by CODEX for lead. Copper result in Site C showed that it is above the limits set by WHO and the sea water source was also beyond the limits set by DENR. All other three sites have lower Cu values.

Table 1. Heavy Metal Content in Sea Salt from Different Locations in Iloilo.

| Location | Cd in mg/kg Mean ± SD | Mn in mg/kg Mean ± SD | Pb in mg/kg Mean ± SD | Cu in mg/kg Mean ± SD |
|---|---|---|---|---|
| Site A | $4.52 \pm 0.19^{c}$ | $2.82 \pm 0.15^{a}$ | $0.57 \pm 0.06^{a}$ | $1.21 \pm 0.00^{a}$ |
| Site B | $3.86 \pm 0.19^{a}$ | $2.93 \pm 0.17^{a}$ | $0.60 \pm 0.05^{a}$ | $1.62 \pm 0.15^{b}$ |
| Site C | $4.10 \pm 0.17^{b}$ | $2.96 \pm 0.16^{a}$ | $0.82 \pm 0.03^{b}$ | $2.70 \pm 0.20^{c}$ |
| Site D | $4.27 \pm 0.26^{b}$ | $3.83 \pm 0.16^{b}$ | $0.57 \pm 0.06^{a}$ | $1.51 \pm 0.33^{b}$ |
| WHO/CODEX Allowable limits | 0.5 | 0.5 | 2.0 | 2.0 |

*Note*: Values are mean ± standard deviation. Values having different superscripts within a column are significantly different at $p<0.05$. Lowest value are assigned with a superscript *a*.

From Table 2, cadmium and copper in all sea water sources have exceeded the limit set by DENR. Only Site B sea water source passed the limit set by DENR for manganese. Site B and D sea water samples passed the limit set by DENR for lead. Site A contain a significant amount of heavy metals. These evaporated water samples from different concentration ponds would basically contain heavy metals.

Table 2. Heavy Metal Content in Sea Water Source.

| Location | Cd in mg/L Mean ± SD | Mn in mg/L Mean ± SD | Pb in mg/L Mean ± SD | Cu in mg/L Mean ± SD |
|---|---|---|---|---|
| Site A | $1.41 \pm 0.01^{d}$ | $0.55 \pm 0.02^{d}$ | $0.24 \pm 0.00^{d}$ | $0.29 \pm 0.01^{c}$ |
| Site B | $0.40 \pm 0.01^{a}$ | $0.15 \pm 0.01^{a}$ | $0.03 \pm 0.00^{b}$ | $0.10 \pm 0.01^{a}$ |
| Site C | $0.84 \pm 0.01^{b}$ | $0.30 \pm 0.01^{b}$ | $0.06 \pm 0.00^{c}$ | $0.19 \pm 0.00^{b}$ |
| Site D | $0.86 \pm 0.02^{c}$ | $0.35 \pm 0.01^{c}$ | $0.01 \pm 0.00^{a}$ | $0.19 \pm 0.01^{b}$ |
| DENR Allowable limits | 0.005 | 0.20 | 0.05 | 0.02 |

*Note*: Values are mean ± standard deviation. Values having different superscripts within a column are significantly different at $p<0.05$. Lowest value are assigned with a superscript *a*.

Table 3 shows the heavy metal content on different iodized salt brands. Brand A has higher Cd, Mnand Cu content. Brand F has a higher Pb content. Other samples did not exceed the allowable limits for lead, copper and manganese but all samples exceeded the limit set by CODEX for cadmium.

Table 3. Heavy Metal Content in Local Iodized Salt.

| Brand | Source | Cd in mg/kg Mean ± SD | Mn in mg/kg Mean ± SD | Pb in mg/kg Mean ± SD | Cu in mg/kg Mean ± SD |
|---|---|---|---|---|---|
| A | Local | 2.26 ± 0.06$^{e}$ | 0.37 ± 0.01$^{e}$ | 0.00 ± 0.00$^{a}$ | 0.07 ± 0.00$^{c}$ |
| B | Imported | 1.93 ± 0.07$^{d}$ | 0.24 ± 0.00$^{a}$ | 0.00± 0.00$^{a}$ | 0.06 ± 0.00$^{b}$ |
| C | Imported | 1.75 ± 0.09$^{c}$ | 0.26 ± 0.00$^{b}$ | 0.00 ± 0.00$^{b}$ | 0.06 ± 0.00$^{b}$ |
| D | Imported | 1.64± 0.05$^{b}$ | 0.28 ± 0.01$^{d}$ | 0.01 ± 0.00$^{c}$ | 0.06 ± 0.00$^{b}$ |
| E | Local | 1.59 ± 0.08$^{a}$ | 0.27 ± 0.00$^{c}$ | 0.00 ± 0.00$^{b}$ | 0.06 ± 0.00$^{b}$ |
| F | Local | 1.68 ± 0.07$^{b}$ | 0.25 ± 0.00$^{a}$ | 0.01 ± 0.00$^{e}$ | 0.06 ± 0.01$^{a}$ |
| G | Local | 1.68 ± 0.11$^{b}$ | 0.29 ± 0.01$^{d}$ | 0.01 ± 0.01$^{c}$ | 0.06 ± 0.00$^{b}$ |
| H | Imported | 1.68 ± 0.09$^{b}$ | 0.25 ± 0.00$^{a}$ | 0.01± 0.00$^{d}$ | 0.06 ± 0.00$^{b}$ |
| WHO/CODEX Allowable limits | | 0.5 | 0.5 | 2.0 | 2.0 |

*Note:* Values are mean ± standard deviation. Values having different superscripts within a column are significantly different at $p<0.05$. Lowest value are assigned with a superscript *a*.

Cadmium was the common contaminant element in both sea salt and iodized salt. Heavy metal contamination of the sea salt may have come from contaminated sea water. Heavy metals are natural constituents of the marine environment which are generally found in very low concentrations. They enter the marine environment through weathering, erosion of rocks, and dust particles. Also, human activity increased the levels of heavy metals contamination in water systems through offshore oil and gas exploration, mine drainage, domestic and industrial (fertilizers, pesticides, paints, leather, textile, and pharmaceuticals) effluents, acid rain and agricultural runoff. Heavy metals in the marine environment are mostly concentrated in coastal areas, near densely populated and industrialized regions. Iodized salt samples have generally lower heavy metal content than sea salt as they undergo purification process. All heavy metals can be toxic when present above threshold concentrations. Once salt contaminated with a heavy metal is consumed and enters the body, these metals are deposited in bone and fat tissues and overlaps other essential minerals. Adverse health effects of heavy metal consumption are kidney dysfunction, liver toxicity, impairment of periphery and central nervous system, increase risk of some cancers and many more (Jang & Hoffman, 2011; Wu, Du, Xue, & Zhou,2010).It could be noted that salt is safe for consumption as long as salt does not exceed the limits set by CODEX and WHO.

## CONCLUSION AND RECOMMENDATION

Based on the study, all the sea salt samples contain cadmium and manganese which are above the allowable limits set by CODEX and WHO. Lead on sea salt samples were below the allowable limit set CODEX. Only site C sea salt samples exceeded the allowable limits for copper set by WHO while all other sea salts have copper content that were below the allowable limits.

For the iodized salt, only cadmium exceeded the limits set by CODEX. Copper, lead and manganese did not reached the limits set by CODEX and WHO.

All sea water source contain cadmium and copper which exceeded the limits set by DENR. The manganese content of Site B sea water source are below the allowable limits while other sites contain this heavy metal which are above the allowable limits. Site B and D sea water sources have lead contents which are below the allowable limits while the other sites of sea water source contain lead which are beyond the allowable limits.

It can be concluded that even though significant amount of heavy metals were detected in sea salt, it cannot generalize that the sea water surrounding Iloilo is contaminated with heavy metals. Factors like soil and pond contamination and pH of soil contribute to heavy metal content (Yong and Phadungchewit,1993).Based on the study, iodized salt contain less heavy metals than sea salt.

It is recommended that the data obtained will be used by the government to confirm the presence of heavy metals in all salt types for food security. It is also recommended that other toxic heavy metals must also be analyzed in food to increase consumer awareness.

Sea salt producers are recommended to make concentration ponds that are either concrete- walled or provide barrier to prevent the soil from contaminating the concentration pond when obtaining their samples for production.

It is recommended to all households, culinary industries and food industries to use salt in moderation.

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