RESEARCH NOTE

CORRELATIONS BETWEEN ZINC AND HEAVY METAL CONCENTRATIONS IN COMMERCIALLY AVAILABLE ZINC OXIDE SOURCES

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ABSTRACT

The study was conducted to determine the correlation between zinc and heavy metal concentrations (lead, cadmium, arsenic) in different ZnO sources. Seven ZnO samples submitted to Laboratory 1 were analyzed for Zn and heavy metal concentrations using atomic absorption spectrophotometry (AAS). Another ten samples submitted to Laboratory 2 were analyzed for Zn using AAS and for heavy metals using inductively coupled plasma–atomic emission spectrometry. Correlations were determined for the data gathered. Concentrations of Zn, Pb, Cd and As ranged from 3.6 to 79.2%, 0 to 1341.2 ppm, 0 to 178.3 ppm, and 0.4 to 12.9 ppm, respectively. Zinc content in different ZnO sources was not correlated with heavy metal concentrations. For Laboratory 1, Pb concentration detected in ZnO was positively correlated ($P<0.001$) with Cd, whereas in Laboratory 2, Pb was negatively correlated ($P<0.001$) with Cd. Arsenic concentration found in ZnO tended ($P<0.07$) to positively correlate with Pb ($r=0.72$) and Cd ($r=0.75$) for Laboratory 1. The present study shows wide variability of Zn and heavy metal concentrations in commercially available ZnO sources. It is recommended that heavy metal concentration in ZnO should be checked regardless of the Zn content.

Key Words: Arsenic, Cadmium, Heavy Metal, Lead, Zinc oxide

INTRODUCTION

Zinc (Zn) is an essential trace element found in all living systems that has important metabolic functions. In weanling diets, it is used at low dosage as a nutrient source and at high dosage as a chemotherapeutic agent that reduces post weaning diarrhea incidence (Mores *et al.*, 1998) and promotes gut health (Hojberg *et al.*, 2005). Studies have shown that pharmacological levels of Zn from zinc oxide (ZnO) at 2,000 to 4,000 ppm improved the nursery pig performance (Smith *et al.*, 1997; Hill *et al.*, 2000; Hollis *et al.*, 2005). However, supplementation at higher concentrations raises issues on feed safety and the environment.

According to US National Research Council (1998), prolonged consumption of high levels of dietary ZnO, depending on the source, can cause Zn toxicity. It is characterized by decrease in feed intake and growth rate (Brink *et al.*, 1959). Furthermore, Zn content of animal manure depends on its concentration in feed and efficiency of feed conversion by the animals (Nicholson *et al.*, 1999).

Aside from toxicity and environmental impact, low quality ZnO sources may have high levels of heavy metals such as Lead (Pb), Cadmium (Cd), Arsenic (As) and Mercury

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(Hg). These toxic metals are known to cause anemia, paralysis and brain damage (FSA Ireland, 2009). Additionally, Cd accumulates in the kidney causing nephrotoxicity and renal tubular dysfunction (Demirulus, 2013). Other damages observed are reproductive system abnormality (Morais *et al.*, 2013), lung damage and skeletal changes (FSA Ireland, 2009).

Analyses of ZnO sources previously reported showed wide range of Cd (484 to 862 ppm) and Pb (2,197 to 14,000 ppm) contents (Animine, n.d.). These levels are higher compared to the maximum allowable limits in swine diets set by European Commission (2013) which are 30 ppm for Cd and 400 ppm for Pb. However, there are limited studies on the quality of commercially available zinc sources for weanling pigs. In addition, there are no studies on the relationship of zinc and heavy metal content of commercial ZnO in the Philippines. Therefore, the objective of this study was to determine the correlation between zinc content and heavy metal (lead, cadmium, and arsenic) concentrations in different commercially available ZnO sources.

MATERIALS AND METHODS

A total of seven (7) ZnO samples were submitted to Laboratory 1 and analyzed for Zn, Pb, Cd and As concentrations using atomic absorption spectrophotometry (AAS). Another ten (10) ZnO samples were submitted to Laboratory 2 and analyzed for Zn using AAS, and for Pb and Cd using inductively coupled plasma–atomic emission spectrometry (ICP-AES).

Using atomic absorption system (graphite or flame), the samples were charred, then ashed to remove the remaining organic residues. The sample ash was digested using hydrochloric acid then purged with a gas carrier. The carrier transported the elements to a heated quartz absorption cell for quantification using Atomic Absorption Spectrophotometer. Results were expressed as ug/kg (ppb) or mg/kg (ppm).

For heavy metal analysis in Laboratory 2, the samples were digested in an acid with hydrogen peroxide treatment. Concentrations of Pb and Cd were measured using Inductively Coupled Plasma – Atomic Emission Spectrometer.

The CORR procedure of Statistical Analysis System (SAS) was used to determine the relationships between Zn and heavy metals (Pb, Cd and As) from each laboratory. A P-value < 0.05 was considered significant.

RESULTS AND DISCUSSION

The samples analyzed in Laboratory 1 had an average Zn content of 58.10% ranging from 3.63% to 79.16% (Figure 1). Average Pb, Cd and As were 294.51 ppm, 31.40 ppm and 5.45 ppm, respectively (Figure 2). On the other hand, the samples analyzed in Laboratory 2 had an average Zn content of 65.28% ranging from 53.80% to 77.40% (Figure 3), while Pb and Cd average contents were 40.42 ppm and 15.58 ppm, respectively (Figure 4).

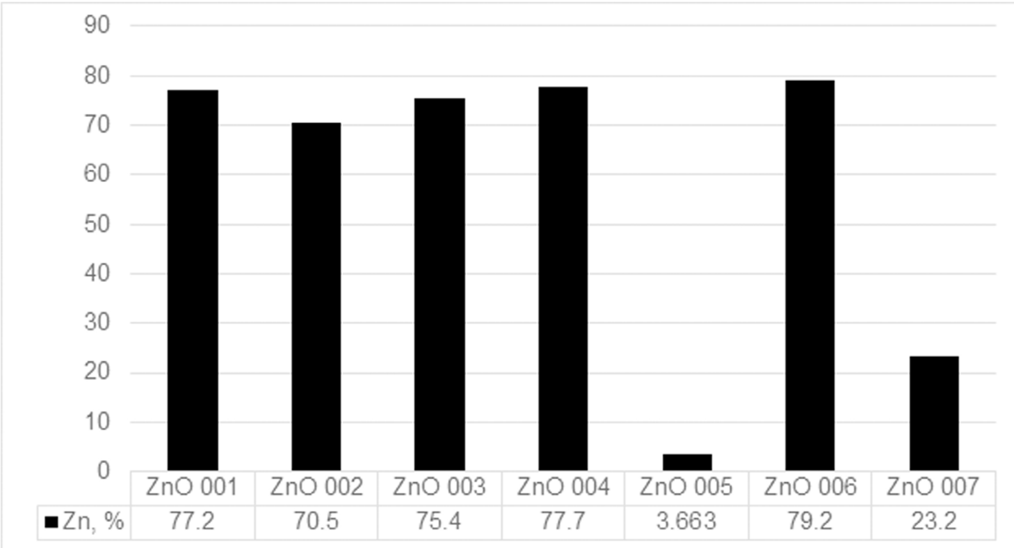

Fig. 1. ***Zinc content of zinc oxide sources analyzed in Laboratory 1.***

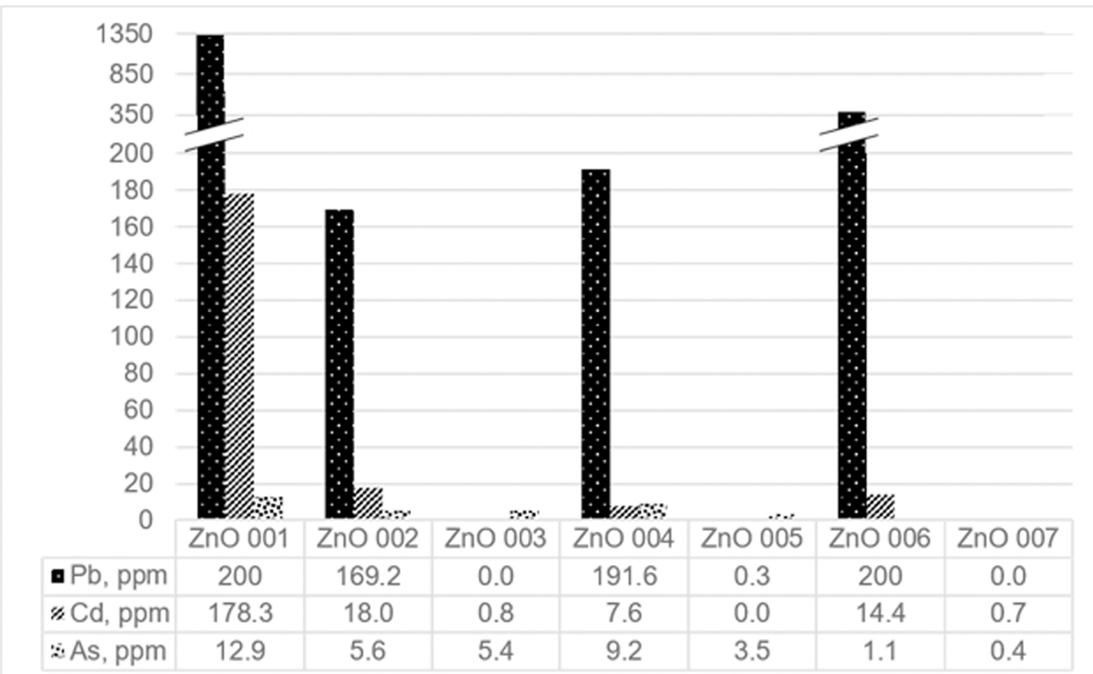

Fig. 2. Lead, Cadmium and Arsenic content of ZnO sources analyzed in Laboratory 1.

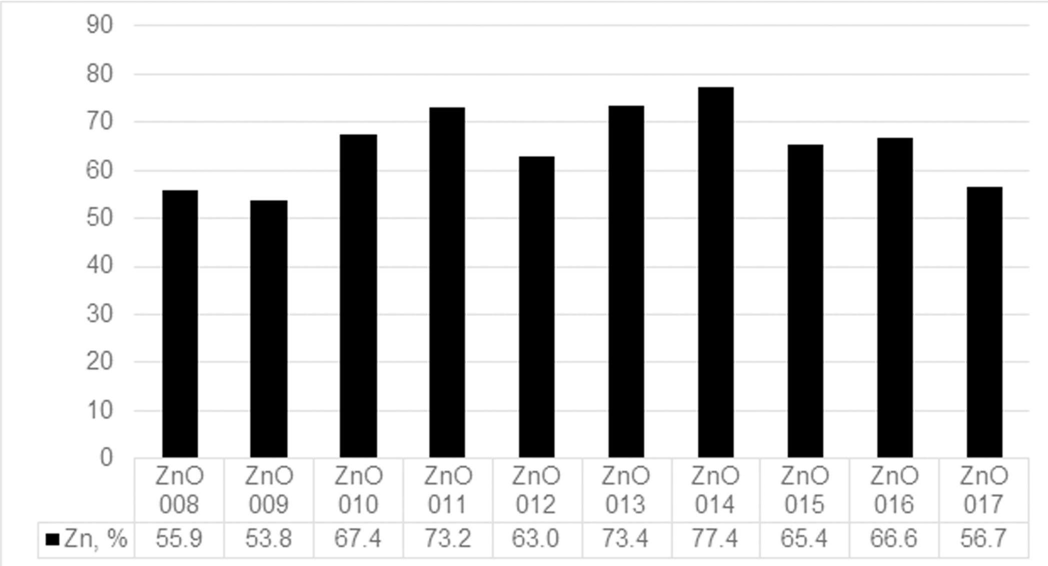

Fig. 3. Zinc content of ZnO sources analyzed in Laboratory 2.

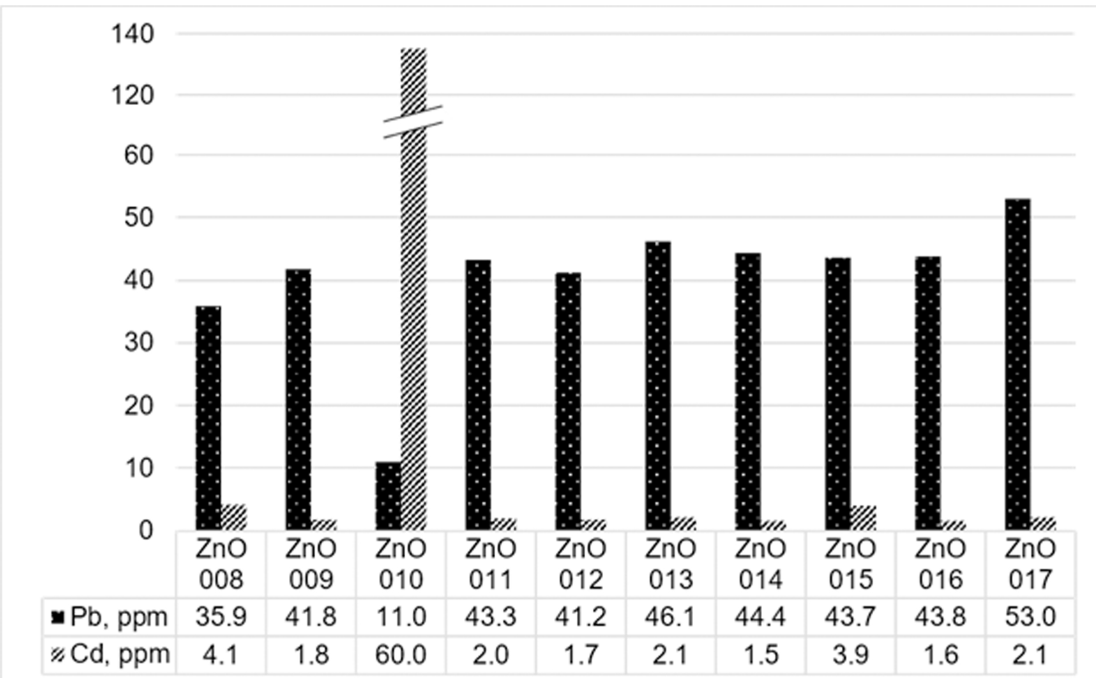

Fig. 4. Lead and Cadmium content of ZnO sources analyzed in Laboratory 2.

Variability of Zn concentrations in ZnO products can be due to differences in the manufacturing process or starting materials (Nasi, 2007; Radzimska & Jesionowski, 2014). Industrially, most ZnO are produced by pyrometallurgical methods (direct or indirect process) or by hydrometallurgical methods. The former use Zn-containing feed materials such as die-casing alloys, Zn ash or galvanized dross that may contain impurities (Cd, Pb, Fe and Al). These metallic Zn materials undergo high temperature processing (>900 °C) with vaporization (Radzimska & Jesionowski, 2014). Zinc melts at 420.0°C (Moezzi *et al.*, 2012) while Pb, Cd and As melts at 327.5°C, 320.9°C and 817.0°C, respectively (Gupta, 2011) resulting to contamination of heavy metals in the final product. While the hydrometallurgical process, also called leaching, includes the selective dissolution of metals from their waste. Aqueous chemicals are used as precursors, and metals are separated at much lower temperatures without vaporization. Special refining processes are conducted if metal acquired still contains impurities (Nasi, 2007) resulting to lower heavy metal content. According to EU standards (Commission Regulation (EU) No 1275/2013), Pb, Cd and As in zinc oxide products should be below 400, 30 and 100 ppm, respectively.

Lead concentration in ZnO sources was positively correlated ($r=0.98$; $P<0.001$) with Cd in Laboratory 1 while Pb was negatively correlated ($r=-0.93$; $P<0.001$) with Cd in Laboratory 2. In addition, As concentration tended ($P<0.07$) to positively correlate with Pb ($r=0.72$) and Cd ($r=0.75$) for Laboratory 1. No relationships were found between Zn and the heavy metals found (Tables 1 and 2).

The difference in correlation can be due to the different analyses done for heavy metal concentrations. According to Thermo Elemental (2011), the most common techniques used to detect heavy metal contents are Flame Atomic Absorption Spectrophotometry (FAAS), Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS) and Inductively Coupled Plasma-Atomic Absorption Spectrometry (ICP-AES). In FAAS, the use of flame restricts the excitation temperature reached by a sample to a maximum of approximately 2600°C (Thermo Elemental, 2011). However, this is inadequate to breakdown compounds of some elements. As a result, FAAS sensitivity for some elements is not as good as other techniques. On the contrary, GFAAS uses electrically heated graphite tube which is heated up to 3000°C (Thermo Elemental, 2011). The longer residence time and high atom density in the tube enhance GFAAS detection limits by a factor of up to 1000x compared to FAAS. Lastly, ICP-AES uses inductively coupled plasma source in which the sample experiences as high as 10,000°C where even the most refractory elements are atomized with high efficiency (Thermo Elemental, 2011). This results to better detection limits than FAAS

Table 1. Relationship between zinc and heavy metal content of ZnO sources analyzed in Laboratory 1.

	Zinc	Lead	Cadmium	Arsenic
Zinc	1.0000	0.4336	0.3332	0.4939
Lead		1.0000	0.9795*	0.7203
Cadmium			1.0000	0.7487
Arsenic				1.0000

*p=0.0001

Table 2. Relationship between zinc and heavy metal content of ZnO sources analyzed in Laboratory 2.

	Zinc	Lead	Cadmium
Zinc	1.0000	-0.0291	0.0853
Lead		1.0000	-0.9277*
Cadmium			1.0000

*p=0.0001

which is typically of the order of 1-10 ppb level. Detection limit is better using GFAAS (usually in sub ppb range), followed by ICP-AES (of order of 1-10 ppb) and finally, FAAS (in the sub ppm range). Moreover, the wide range of ZnO concentration can be the reason for the lack of correlation to heavy metal contents.

In conclusion, there is wide variability in the quality of ZnO in terms of Zn concentration and the presence of heavy metals. It is recommended that commercially available ZnO sources should be checked for heavy metal concentrations regardless of the Zn content.

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