Le Corps professoral de
Gembloux Agro-Bio Tech - Université de Liège vous prie
de lui faire l'honneur d'assister à la défense publique de la dissertation originale que

Madame ZHOU Xuewei,

Titulaire d’un diplôme de _master of agronomy_,

présentera en vue de l’obtention du grade et du diplôme de

.DOCTEUR EN SCIENCES AGRONOMIQUES ET INGENIERIE BIOLOGIQUE,

le 28 octobre 2019, à 14h00 précises (personne ne sera admis après cette heure),
en l’auditorium ZT1 (Zootechnie, Bât. 1),
Passage des Déportés, 2, à 5030 GEMBLOUX.

Cette dissertation originale a pour titre :
« _Heavy metals in Chinese raw cow milk: spatial distribution and relationships with silage and environmental factors_ ».

Le jury est composé comme suit :

Président : Prof. Y. BECKERS, Professeur ordinaire,
Membres : Prof. H. SOYEURT (Promoteur), Prof. J. WANG (Copromoteur - CAAS, Chine), Prof. G. LOGNAY, Prof. K. DAS, Prof. M. HANIKENNE, Prof. N. ZHENG.
Summary

Milk and dairy products play important roles in human diets. Owing to the increasing consumption of milk and dairy products in China, the enhanced national production of milk and the presence of polluting industrial activities that could directly or indirectly contaminate milk with heavy metals, there is a need to screen for the presence of heavy metals and to assess the potential health risks of consuming contaminated milk. Therefore, this thesis conducts a large-scale research to study the spatial variability of heavy metals contents in raw cow’s milk produced in the 11 main producing areas in China. This research also estimates from a limited set of records the relationships between the content of heavy metals in individual cow’s milk, drinking water, feed and soil to isolate pathways potentially responsible for the milk contamination. Moreover, this thesis aims also to assess the human health risk of consuming contaminated milk by calculating using theoretical approach the hazard quotient (HQ). As the analysis cost to measure the contents of heavy metals in milk is high, there is an interest to find a cheap proxy. This one could be related to the milk composition. Therefore, the correlation values between the heavy metals’ contents in milk and the main milk components were also estimated in this thesis.

The concentrations of heavy metals were measured in 1,043 bulk milk samples, 60 individual cow milk samples, 46 drinking water samples, 6 silage and soil samples and 40 TMR samples. All samples were analyzed by inductively coupled plasma mass spectrometry after microwave assisted acid digestion, except for soil samples, which were analyzed by atomic absorption spectrometry and atomic fluorescence spectrometry. The main results of this thesis are as follows:

1. The average concentrations of Pb, As and Cd in bulk milk were 1.74 μg/L, 0.32 μg/L and 0.05 μg/L, thus suggesting limited cause for concern regarding heavy metal contamination in milk produced in China. Only 12 bulk milk samples (1.15%) exceeded the maximum residue limit (MRL) of Pb set by the European Union. There is no expected health risk when those average and highest levels were used to calculate HQ values. Indeed, those values were always lower than 1.

2. Regional variability was observed in the Pb, As and Cd contamination in milk. A higher heterogeneity of heavy metal content in milk was observed within areas than between areas. The content of Pb and Cd in individual milk samples from industrial areas was significantly higher than that in agricultural areas, but the content of As was significantly lower. This result suggested that industrial activities (i.e., steel production, waste incineration plant and cement plant) lead to potential Pb and Cd contamination in milk, thus confirming the need to know the micro-environment of the farm to interpret the observed contents of heavy metals.

3. The ingestion of contaminated feed, water, and soil by cows can induce the production of contaminated milk. Weak correlation values were obtained from As concentrations between water and bulk milk (r ranged from 0.12 to 0.45). As content in individual cow’s milk samples was positively correlated with the content in water (r=0.37). Conversely, Cd in milk was negatively correlated with Cd in water. Nearly no relation (r ranged from -0.03 to 0.09) was found between Pb levels in water and milk. This result indicated that drinking water may be the main source of As contamination in raw milk. Weak positive correlations were observed between heavy metals in milk and silage. The content of Pb in individual cow milk samples was positively correlated with Pb in silage (r=0.54). Heavy metals in silage appeared to be the main source of heavy metals in raw milk. Moderate positive correlation values were found for Cr (r=0.60) and Cd (r=0.66) between milk and soil, and negative values were observed for Cr (r=-0.60) and Cd (r=-0.75) in water. Those correlations suggested that water and soil contaminate milk differentially.

4. No strong relationships were observed between the content of heavy metal and milk composition. However, weak positive correlations were found between Pb and protein in milk (r=0.11), and Cr and protein in milk (r=0.18). Cd content in individual cow’s milk was weak positively correlated with lactose. Beyond these, heavy metals and milk composition showed zero or negative correlations. Thus, milk protein appeared to be more affected by heavy metal pollution than other milk components.

In conclusion, this thesis highlights the presence of heavy metals at low quantities in milk produced in China. Therefore, there is a need to define a sampling protocol to screen dairy farms with a potential to produce contaminated milk, to ensure that high quality milk is provided to consumers. Unfortunately, the results obtained in this thesis were not sufficient to propose a detailed sampling procedure, because information on the micro-environment (such as the presence of industrial activities or the type of industry) around the farm was lacking. Such knowledge was highlighted in this thesis to be the most important factor to illustrate the sources of heavy metals in raw milk. Moreover, there is also a need to increase the sample size to provide higher confidence in the relationships described in this thesis.