SUMMARY

Key words: mineral oils hydrocarbons, pollution, feed, milk, agri-food chain

Modern pollution and current pollutants present numerous challenges for the agri-food sector, even more so for animal production. The legislative provisions on modern contaminants are still insufficient, they are limited to the food sector and underestimate the importance of animal nutrition in obtaining safe productions, which makes it difficult to monitor a potential contamination and apply specific prevention measures.

Few approaches was developed regarding the incidence of mineral oil hydrocarbons in feed because the problem of this contamination caught the attention internationally a few years ago, even more so, in our country.

The evolution of the issue regarding modern pollution and contamination in the agro-food chain led to a series of investigations regarding the risks of exposure to environmental contamination. Important carcinogenic and genotoxic characters, as well as a high potential for bioaccumulation of contaminants in human and animal organisms, have been highlighted for mineral oil hydrocarbons.

Insufficient data and toxicity of modern contaminants have led to the need to systematically and critically investigate the incidence of contamination episodes with mineral oil hydrocarbons in the animal production.

Through the analytical association of some concepts and ideas, an intense research activity was carried out for monitoring and quantifying the mineral oil hydrocarbons, in order to evaluate the possibility of their migration from feed to milk, as a possible result of metabolic transfer from the animal body.

Through specific extraction and purification procedures and the application of the coupled LC-GC-FID detection technique, feed and milk sampled from three farms located in geographical areas selected according to expected level of pollution were analyzed, in order to monitoring, quantifying and confirming the presence of mineral oil saturated (MOSH) and aromatic (MOAH) hydrocarbons.

In order to evaluate the factors that could affect the innocuity of feed and milk and to understand the mechanisms of the transfer of contaminants from feed to milk, the research was carried out towards specific objectives, by analyzing the level of contamination in relation to expected level of pollution in the farms, characterizing the contamination profile and developing effective strategies to reduce pollution and maintain a good relationship between animals and environment.

The PhD thesis "***Contributions to assessment of the transfer of some pollutants from feed into cow's milk***" was structured in two parts, including a total of seven chapters, 43 tables, 54 figures and 274 bibliographic titles, which have integrated into the dynamics of the thesis, study of the literature referring to addressed issue, own research, conclusions, recommendations, but also originality, a selection of the innovative contributions of the thesis and bibliographic references.

Current data from literature and specific research were included in the first two chapters that made up the first part of the paper.

In the first chapter, the particularities regarding the relationship between environmental pollution and animal production were presented, focused on the main pollutants and contaminants with a high incidence on the agro-food chain, to which were integrated some aspects regarding the chemical composition and the transfer of substances from food to the animal body and to the animal productions.

In the second chapter, the main particularities regarding the incidence of a new class of contaminants, mineral oil hydrocarbons, were described, with an emphasis on their toxicity on animal and human organisms and on the possibilities of confirming their presence in vegetal and animal production.

The own contributions of the PhD thesis includes five chapters in which were presented the purpose and organization of research, was described the methodology for confirming the contamination of feed and milk with mineral oil hydrocarbons and were materialized the results of the research in order to evaluate the potential of the transfer of pollutants along the agri-food chain, clarifying the mechanisms of the transfer of contaminants from feed to milk.

The third chapter argues the purpose, objectives, motivation and applicability of the research and briefly describes the organization of research, with an emphasis on selected organizational framework, the study material and the detection technique for confirming the presence of contaminants in the samples.

The results of the research, integrated in the last three chapters, present in an objective way, the most relevant aspects identified following the monitoring and confirmation of presence of saturated and aromatic mineral oil hydrocarbons in the feed and milk samples of the farms.

Based on the data obtained from the research carried out in the farms selected by geographical areas (mountain, rural, urban), strategies were developed to confirm the contamination of feed and milk. The results obtained were formulated according the proposed objectives, as follows:

- The methodological framework of the research was fixed and sources of pollution and risk factors regarding the contamination were evaluated.

In relation to potential level of pollution expected in selected geographical area, the three farms were characterized:

- Farm S-Mo = Dairy cattle farm, with low potential pollution level (S), located in mountain area (Mo);
- Farm M-Rr = Dairy cattle farm, with medium potential pollution level (M), located in the rural area (Rr), but located according to the main pollution objectives in the neighboring urban area, on the dominant direction of the wind;
- Farm R-U = Dairy cattle farm, with potential high level of pollution (R), located in the urban area (U), in the vicinity of an area with numerous sources of pollution, air and land transport, industrial activities or waste being the most common.

For all three farms, through individual observation and by elaborated sampling sheets, was followed out the activity, feed bases, specifics of the feeding or care activities of vegetal crops and soil were monitored and analyzed.

- The crude chemical composition of feed and milk was determined and monitored parameters were comparatively analyzed, in relation to the specifics of feeding of animals in

each farm. Among the crude chemical components, fat content has had particular applicability in relation to the study of contaminants.

- The presence of MOSH/MOAH in feed samples was monitored and confirmed and contamination profile was characterized in relation to the implications of polluting or contaminating factors; the results obtained allowed the comparative analysis of feed contamination from the three farms (mountain, rural, urban).

For both MOSH and MOAH, quantitative and confirmatory results were generally obtained for the presence of important contaminants to prove the reliability of the LC-GC-FID detection method used, which demonstrated good performance in terms of quantification of results.

Evaluation of contamination levels of feed confirmed the presence of MOSH and MOAH generally for all types of feed analyzed, differences being given by the specifics of each farm in relation to exposure to different sources of pollution, the positioning of the farm and the location of crops from which feed was sourced or the degree of technologization in farms.

Following the quantitative analysis, it was observed that the results regarding MOSH and MOAH concentrations varied widely; feed samples had an average MOSH contamination between 11,4–81,4 mg/kg and a detectable MOAH level between 0,6–4,6 mg/kg; except for four feed types (1–M-Rr farm, 3–R-U farm), all other samples had levels of MOSH and MOAH several times above the EU-RL recommended limit of 0,5 mg/kg.

Chromatographically, the contamination profiles also confirmed the presence of MOSH and MOAH in feed samples analyzed, but due to the instability of pollution, the relationship between contamination level of feed, location of vegetal crops and associated pollution sources remains subjective.

The results obtained for S-Mo mountain farm showed that the contamination level of feed was between 21,6–27,4 mg/kg MOSH and 1,2–1,6 mg/kg MOAH. In M-Rr rural farm, feed samples showed an 11,4 mg/kg, up to 35,0 mg/kg average level of MOSH contamination, while MOAH contamination was minimum, up to 2,5 mg/kg. For the R-U urban farm, the level of feed contamination ranged from 16,9–81,4 mg/kg MOSH to 0,5–4,5 mg/kg MOAH.

Specifically, the considerable level of MOSH/MOAH contamination of feed was generally attributed to land and air traffic, industrial activities, areas with mining activities, as well as technological contamination through emissions and technical fluids of agricultural equipment and machinery used for obtaining feed.

Evaluating the pollution and contamination factors, for all three farms, it was highlighted that technologically, the operations applied to vegetal crops did not have a considerable impact in terms of contamination of feeds.

In relation to pollution, the level of contamination of feed in each farm was not entirely proportional to the degree and intensity of exposure to sources of pollution identified in the geographical area studied. For both MOSH and MOAH, the lowest level of feed contamination was found for the rural farm M–Rr, followed by a higher contamination found for the feed of mountain farm S-Mo, the highest level of contamination being attributed to feed from urban farm R–U.

- The presence of MOSH and MOAH in samples was monitored and confirmed and contamination profile was characterized in relation to the implications of different pollutant or contaminant factors; the results obtained allowed the comparative analysis of milk contamination from the three farms.

The obtained results revealed particular levels of contamination with MOSH/MOAH for all four analyzed milk samples, with values between 3,3–9,9 mg/kg MOSH and 2,6–5,7 mg/kg MOAH. Small differences were noted between the farms, with all milk samples showing a level of MOSH and MOAH contamination considerably higher than the EU-RL recommended limit (0,5–1,0 mg/kg).

For identify the specific sources of contamination, as far as possible, the quantification of MOH was carried out from the contact materials in which mineral oils are found and with which the milk came into contact. An important contamination given by contact materials was highlighted, supported by a similar contamination profile, confirmed in analyzed milk samples.

- Strategies were developed to confirm the transfer of MOSH/MOAH from feed to milk, by analyzing average MOSH/MOAH contents and analyzing contamination profiles to identify common interferences.

Similarities between contamination profiles and a similar distribution of MOSH/MOAH were highlighted for several feed–milk sample groups; even in the absence of a complete match of contamination profiles, the similar distribution of MOSH/MOAH contaminants in the same molecular range ($n–C_{16–25}$) observed in feed and milk samples showed a model of metabolic migration of contaminants from ingested feed into milk and thus indicated common contamination conditions.

The estimation of possibility of metabolic transfer of contaminants from feed to milk, based on quantitative results obtained, generally showed a medium to low migration of tracked contaminants. Based on the evaluation of contamination profiles, it was appreciated that the transfer of contaminants was more evident for mountain farm S-Mo, followed by rural farm M-Rr and, finally, the urban farm R-U.

Common interferences confirming the metabolic transfer of MOSH/MOAH in milk, were observed especially between S-FN natural hay samples and $S\text{-}L_i$ winter ration milk from mountain farm; corn grain samples M-PB, soybean meal M-SS, mixed feed M-AU and milk samples M-L of rural farm and also corn silage samples R-SP, alfalfa silage R-SSL, corn grain R-PB and R-L milk samples of urban farm.

The valorization of the results was achieved by obtaining specific data in different research areas; beeing comparable to previous results obtained in similar research.

The strategic management through which connections were made between the obtained results allowed highlighting the transfer of contaminants from feed to milk based on common interferences and also, was highlighted the ability to identify optimal solutions to address feed safety issues as an essential factor for safety animal productions.

Being substantiated on the basis of well-argued specialized references and adapted in such a way as to provide original content and added value to international research, this doctoral thesis represents the primary form of an achievement that, through its results, can serve to implement good production practices for minimizing the risks of contamination and can open new horizons of collaboration with companies with similar concerns in the field.