

CONTROL OF ORGANOCHLORINE PESTICIDES IN AGRICULTURE AND ANIMALS: OFFICIAL MONITORING IN ANIMAL PRODUCTS IN BRAZIL BETWEEN 2004 – 2013

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Introduction

As a group, organochlorine and other halogenated hydrocarbons are environmentally persistent pesticides. Related groups of compounds include the PCB (polychlorinated biphenyls), the dioxins/furans and the polycyclic aromatic hydrocarbons (PAH). Arguably, their extended monitoring in food matrices is of key importance from a public health perspective.

In the case of dioxins/furans¹, food is the major exposure route for human beings, mainly through meat/beef and dairy products (87.1%), followed by vegetables (5.1%) and fish (1%). Overall, such foods contribute an estimated 92.2% of human exposure to dioxins/furans, whereas only 7.4% comes from ingestion of dust (4.6%) or by inhalation (2.8%). Herbicides^(a) presence in milk products has already been reported in Europe and USA and also on fish/shellfish in Japan. Besides, organochlorine compounds are also quoted as the most relevant residues in milk, meat/beef, poultry/eggs¹⁵, in the latter also as a direct source of PCB to the general population¹⁰.

Food is also a central vehicle for polycyclic aromatic hydrocarbons (PAH). PAH originate from incomplete combustion of organic matter such as tobacco, coal, charcoal, diesel and wood, being then spread by air and atmospheric precipitation, eventually reaching water, soil, produce and animals^{11, 14}. As lipophilic molecules, PAH accumulate in animal fats, posing food public health concerns. Specifically, such PAH accumulation mean that their concentration in milk can be five times greater than in the dry matter of the respective animal feed⁹. In contrast, polychlorinated biphenyls (PCB) may derive directly from silo sealants, inks, waste from mineral oils, heat exchangers and electric transformers¹⁶.

Dioxins, furans have high toxicity, being also associated with cancer promotion, immunodeficiency, endocrine and reproductive systems disruption/developmental disabilities, in addition to causing negative neurological, hepatic, cardiovascular and dermatologic effects¹. PCBs are probably carcinogenic to humans¹⁶. For the PAH group, there are 189 compounds considered as hazards in the class of atmospheric pollutants according to the US legislation. Several PAH are known lung carcinogens, or suspected agents for cancer of the bladder, larynx and prostate, besides being endocrine disrupters¹¹.

Overall, organochlorine pesticides are synthetic, while dioxins and furans can be generated as by-products of industrial manufacturing processes and combustion¹.

Therefore, such compounds can accumulate in the air, water and soil as a result of industrial and agricultural activity, including effluent management protocols and possible environmental accidents. From a public health standpoint, it is important to assess the translocation patterns of those compounds in the biosphere, because their migration from environmental sources to vegetables and animals precedes food contamination.

In Brazil, the Ministry of Agriculture, Livestock and Food Supply (MAPA) enforces extensive regulation concerning organochlorine pesticides. In 1971, both the production and the trading of animal antiparasitics containing DDT or BHC (Ordinance n°356) were banned. Prohibition also included organochlorines for crop pesticides². Since the implementation of the National Program for the Control of Biological Residues (PNCRB) in 1979, MAPA has been systematically searching key animal and plant food matrices for organochlorine pesticides, in addition to antibiotics, organophosphates/carbamates, hormones, growth promoters, toxins, and inorganic contaminants (including heavy metals). Such official surveys are intended to estimate the prevalence

(^a)In a report from Canada 70% of pesticide used were herbicides, of which 30% were triazine¹⁵

and incidence of residues and contaminants in each region of the country⁴ in order to instruct possible additional regulatory protocols.

As of 1985, Ordinance n°329⁵ further restricted the usage of organochlorine compounds. Since then, all trading, use and distribution of such compounds has been forbidden.

The PNCRB initially targeted meat, beef, and pork, including poultry. Starting 1986, the approach has been extended to include all products of animal origin. Accordingly, Ordinance n° 51⁶ triggered a migration from a specific control program to a national control plan for biological residues in products of animal origin, aiming at assessing and verifying the effective adoption of Good Agricultural Practices as a central tool to maximize food safety. As it turns out, in the recent years the PNCRB has been referred instead by the acronym PNCRC (National Control Plan for Residues and Contaminants), emphasizing its ever-increasing scope, not only to encompass drug and pesticide residues, but also chemical contaminants.

Additional official restrictive policy took place later, in 1986, by means of Ordinance n°191⁷, which forbids the manufacture/importation/trade of veterinary products containing organochlorines (mainly DDT, lindane and total HCH). Relative to ordinance n°356/1971², such increased regulation bans all organochlorines (not just DDT and BHC), and includes controls and policies for imported products.

Currently, a few organochlorine pesticides are legally allowed only for ant control (aldrin e dodecachlor); for termite control in reforestation (aldrin), and for government-enforced control programs of specific vector-borne diseases⁵.

This work seeks to present and discuss the results of the monitoring subprogram of PNCRC (2004-2013) as a means to maximize safe levels of consumer exposure to organochlorine pesticides in foods of animal origin produced in Brazil.

Materials and methods

Given a binomial distribution for the sought event (violation / non-violation), sample sizes (n) for random stratified sampling from an infinite population (defined as $N > 10,000$ animals for any species/food matrix), are calculated to detect at least one violated sample, assuming a low hypothesized prevalence (for instance 1-2%) and a statistical confidence (α) of 1-5%^(13, p. 158, 8, Appendix A, Table 1).

Briefly, assays consisted of SPE (Solid Phase Extraction) with alumina, followed by gas chromatography with electron capture detection (GC-ECD). This method was officially validated according to national and international standards, achieving a limit of quantification (LOQ) $< 50\%$ of the Maximum Residue Limit (MRL) for each contaminant (LOQ ca. $50 \mu\text{g}\cdot\text{kg}^{-1}$).

Data on the total number of analysis by year in each animal species and by group of monitored compounds were gathered from open access documents published in the Official Gazette (DOU). Electronic records were generated in correspondence to year and respective legal documentation for further analysis.

Annual results (2004-2013) for the number of analysis and the number of violations related to organochloride residues and contaminants (organochlorine pesticides, polycyclic aromatic hydrocarbons – PAH, polychlorinated biphenyls – PCB, dioxins/furans) were assessed using basic Excel™ spreadsheet analysis tools. Two major composite groups were defined, with analysis results being assigned either to "organochlorine" or to "dioxin" group.

Results and discussion

The animal species included in the monitoring of 2004-2013 for residues of organochlorine pesticides are fowl, beef and dairy cattle, equine, swine and fish (either caught or farmed). Honey was also included.

Annually issued legal documents for the PNCRC designate either chlorines, organochlorine pesticides, other halogenated compounds, HPA and PCB as simply "organochlorines", whereas dioxins and furans are referred simply as "dioxins".

Considering the 6,162 samples randomly taken from relevant populations of fowl, cattle (beef and dairy), swine and horses, raised in Brazil between 2004-2013, violation prevalence for organochlorines was lower than 1% (with 99% statistical confidence), as shown by more than 459 assays performed for such species - albeit less than 459 assays were performed for fish (264 for farmed and 141 for wild caught fish) or honey (137). Thus, during 2004-2013, excluding fish, sampling included a total of 5,620 animals [6162- (137 + 141 + 264)].

Hence, the 5,620 assessed samples for organochlorine violations, yield the prevalence of such violations in Brazilian animal products to be $< 1\%$ (with 99% statistical confidence). This evidence is further reinforced given that such sampling plan exceeds the minimum of 4,603 samples as required by CAC 71 (FAO, 2009). Similarly, it was demonstrated that the prevalence of violations in honey and fish is less than 5% (99% statistical

confidence), considering a total of 137 organochlorine determinations in honey, and 141 and 264, respectively, for caught and farmed fish.

Overall system operation, especially reliability of sample collection and traceability standards, are ensured by MAPA's customized IT system (SISRES), allowing target populations to be systematically monitored by MAPA's Federal Inspection Service (SIF). Analytical competence has been long achieved by the National Network of Agricultural Laboratories, which has been substantially strengthened since 2006 for unequivocal international recognition¹² and under ISO 17025/2005 standard. This evidence helps placing the Brazilian PNCRC, and its results, on par to the best programs currently available worldwide.

The prevalence of organochlorine residues in animal products in Brazil is compatible with a satisfactorily controlled system to manage the use of these compounds in the production chain (insecticides, herbicides, fungicides) as indeed not a single violation occurred for any of the 378 monitored compounds, among organochlorines, PAH, PCB, dioxins and furans. The maximum violation prevalence detected is 0.1% (with 99% certainty) in cattle products (beef and dairy), horses and pigs, and a maximum of 5% for honey and fish (caught and farmed). Nevertheless, ever-increasing, continuous efforts in official risk analysis policies should provide continuous improvements to such achievements.

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