ON THE IDENTIFICATION OF PCDD/F SOURCES IN FREE-RANGE CHICKEN EGGS

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Introduction

It is generally accepted that consuming soil particles is the main pathway of PCDD/F to free-range chickens. However additional potential PCDD/F sources such as feed, ash from open burning of household waste, contaminated building materials of henhouses may also be available to chickens [1]. To distinguish between these pathways congener profile can be used which is a valuable tool for identification of contamination sources. However, comparing the commonly used full 2,3,7,8-substituted congeners profiles does not always lead to correct source identification partly due to congener-specific bioaccumulation. As the extent of differential transformation between congeners mainly depends on the degree of chlorination, differences in weathering and bioaccumulation between 2,3,7,8-chlorinated congeners of the same homologue class are likely to be smaller than differences between different homologue classes. To somewhat neutralize the effects of differential weathering and bioaccumulation resulting from a degree of chlorination among environmental samples a so-called "relative homologue" standardization method was proposed. Each 2,3,7,8-substituted congener concentration is divided by its respective homologue class concentration (e.g., 2,3,7,8-TCDD is divided by the total TCDDs, 1,2,3,4,7,8-HxCDF is divided by the total HxCDFs). OCDD and OCDF are divided by the total dioxins and furans, respectively [2,3]. Also, separate assessment of the individual homologue classes was suggested. In particular, using just HxCDD/F data as opposed to seventeen 2,3,7,8-substituted congeners was shown to give a better match between soil and eggs profiles [4]. However bioaccumulation factors of congeners within the same homologue class can differ more than two-fold [5,6]. Thus, this approach does not neutralize the effects of congener-specific bioaccumulation completely. The aim of the present study was to assess the presence of additional contamination sources available to free-range chickens by analyzing the profiles of penta-, hexa- and hepta-chlorinated congeners separately.

Materials and methods

Sample information and the details of sampling, extraction, clean-up procedures and quality assurance/quality control details and calculated mean bioaccumulation factors for individual congeners (BAFs) were previously reported [5]. Briefly, free-range chicken eggs and soil available for chickens to forage on were sampled from 36 private households in different Vietnam provinces. Also, samples of ash from open-burning of household waste were collected from 2 households (Tan Phong and Hoa An districts in Bien Hoa city, Dong Nai province). Eggs were hard-boiled, freeze-dried, spiked with a mixture of ^{13}C-labelled standards and extracted via flow solvent extraction with a mixture of hexane and ethanol (1:1). Extracts were consequently cleaned-up on an activated carbon column (AX-21 Anderson Development Co.), a multi-layer and alumina columns. Soil and ash samples were extracted with a mixture of toluene and acetone (9:1) via flow solvent extraction and cleaned-up on a multi-layer, activated carbon (AX-21) and alumina columns. Extracts were analyzed for 17 2,3,7,8-substituted PCDD/Fs using HRGC-HRMS method on Agilent Technology 7890 chromatograph, connected with high-resolution mass spectrometer Waters Autospec Premier.

Results and discussion

Analysis of PeCDD/F and HxCDD/F profiles revealed close match between free-range chicken eggs and respective soils with expected shift in eggs towards congeners with higher BAFs (1,2,3,7,8-PeCDD for penta-chlorinated congeners and 1,2,3,6,7,8-HxCDD for hexa-chlorinated congeners) in the majority of households (some examples are presented in fig.1).

However, in several households an inconsistent with BAFs shift towards some furans was observed (examples in fig.2(a)) suggesting an input of some additional PCDD/F sources apart from soil. In fig.2(b) profiles of the most likely sources: open burning[7], rice straw burning[8] and Arochlor mixture[9] are presented. Combustion of field residues directly after harvest and open burning of household waste are common practices in Vietnam and were shown to be major sources of PCDD/Fs in ambient air in rural areas[10]. Rice straw burning source is expected to be more evenly contributing to overall soil contamination and could not be considered as additional PCDD/F source for chickens. Thus, consumption of ash particles from open burning of waste by chickens seems to be the most probable reason of the observed shift in profiles.

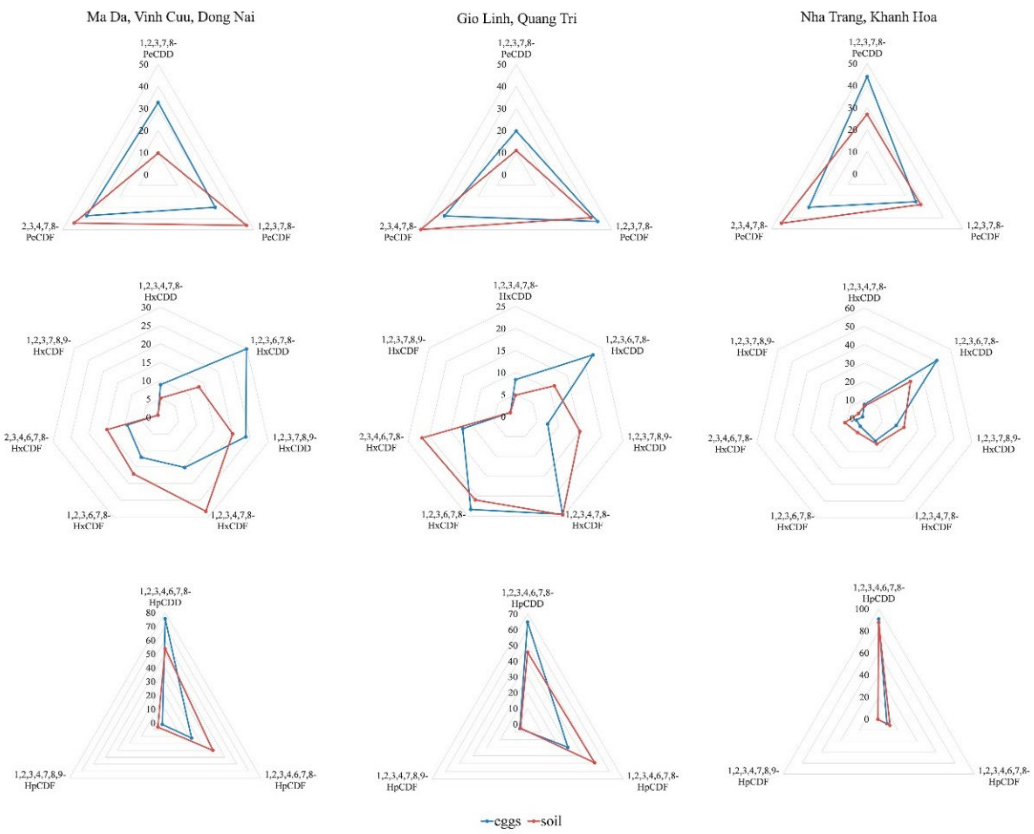

Figure 1. Profiles of 2,3,7,8-substituted penta-hexa-chlorinated and heptachlorinated dioxins and furans in soil and egg samples with typical shift towards congeners with higher BAFs.

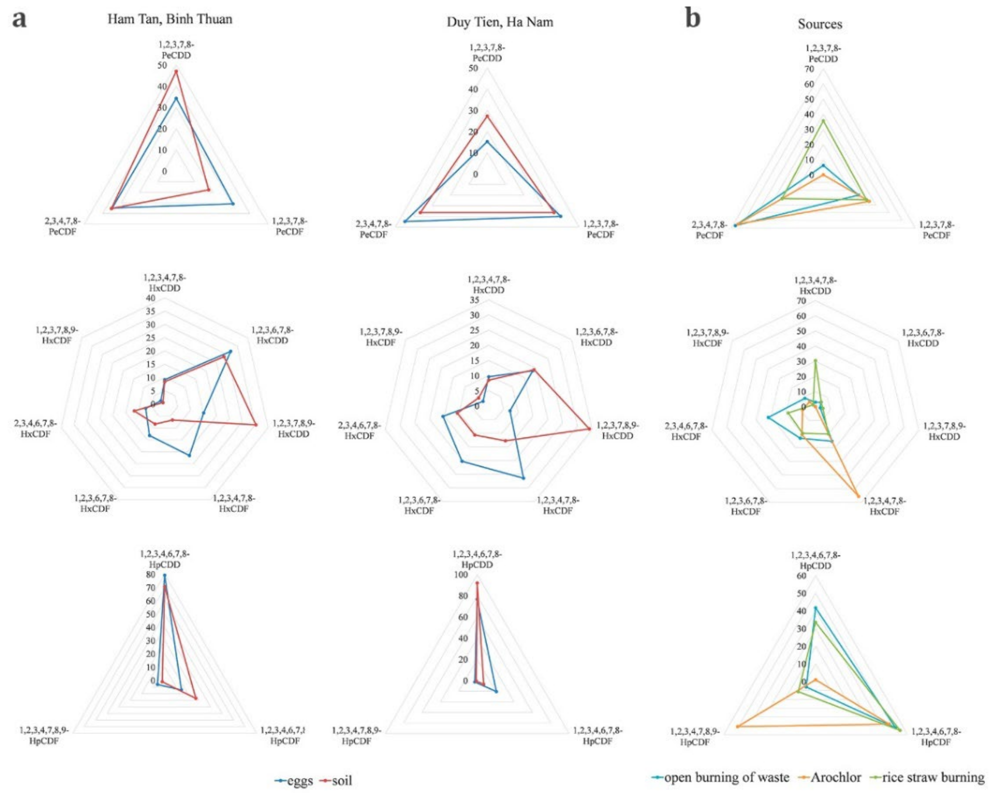

Figure 2. Profiles of 2,3,7,8-substituted penta-, hexa and heptachlorinated dioxins and furans in soil and egg samples exhibiting inconsistent with BAFs shift towards some furans suggesting additional source (a) and potential sources profiles (b): open burning of waste in barrels[7], Arochlor[9] and rice straw burning[8]

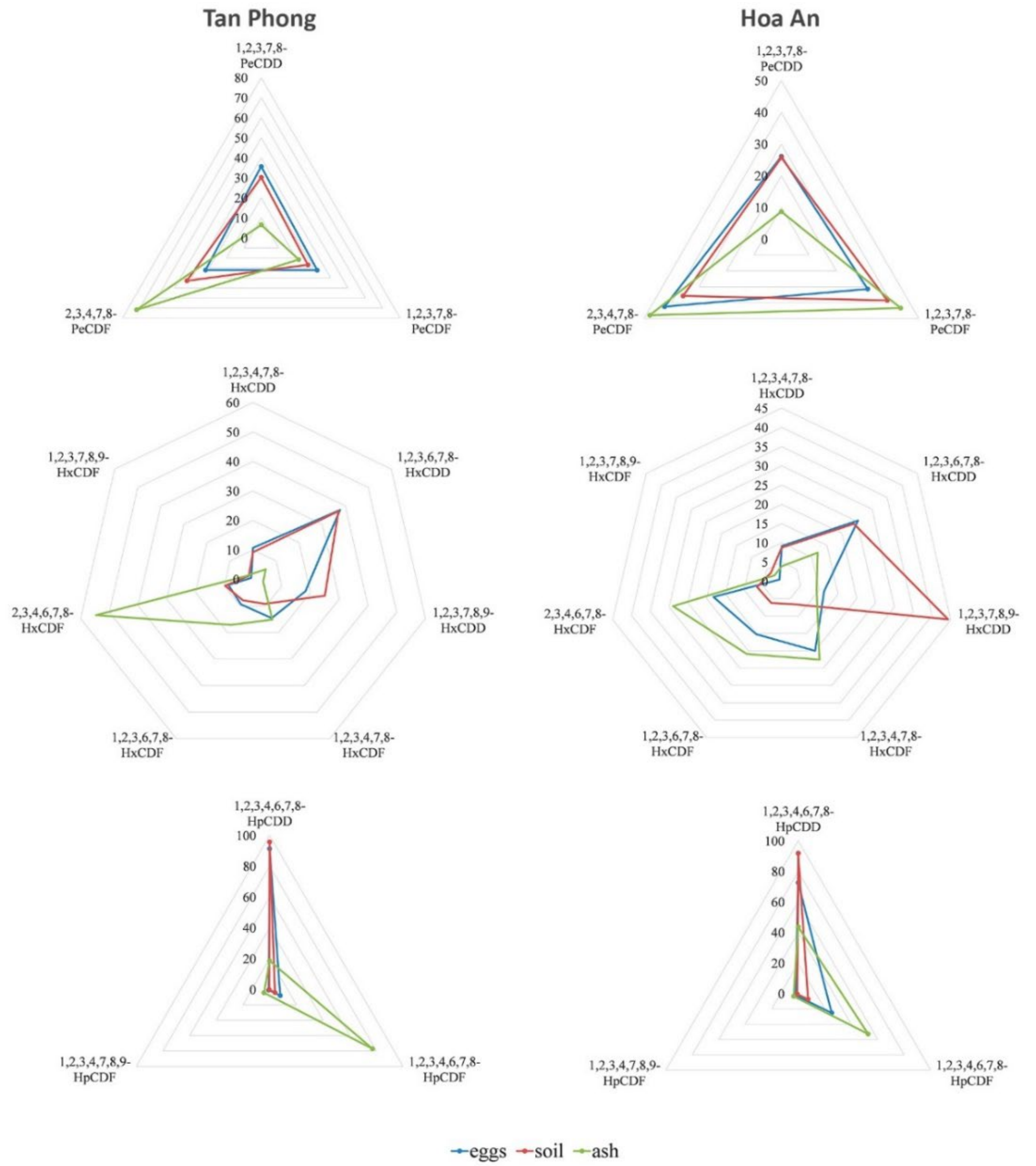

Figure 3. Penta-, hexa- and hepta-chlorinated dioxins and furans profiles in free-range chicken eggs, soil and ash from open burning of domestic waste from two households in different districts of Bien Hoa city, Dong Nai province.

In fig.3 profiles in eggs, soil and ash from two households in Bien Hoa city are presented. Eggs from both households are characterized by high PCDD/F levels (7.4 and 11 pg WHO-TEQ_{2005}/g lipids in Hoa An and Tan Phong districts respectively) exceeding current EC limit for eggs and egg products. In Hoa An district a clear shift in egg profile towards ash profile is observed, indicating ash contribution to total egg contamination. Whereas in Tan Phong district egg profile is closer matched to soil profile, suggesting that ash consumption, if present, does not affect substantially total contamination of eggs.

Analyzing profiles of individual eggs within separate households may also reveal individual chicken's feeding habits. In fig.4 eggs 3 and 4 exhibit a HxCDD/F profiles with a shift to 2,3,4,6,7,8-HxCDF and HpCDD/F profile with a shift towards 1,2,3,4,6,7,8-HpCDF, characteristic to open-burning pattern. These eggs also have two-fold higher TEQ levels (8.7 and 8.4 pg WHO-TEQ_{2005}/g lipids) compared to other three samples (4.0-4.2 pg WHO-TEQ_{2005}/g lipids). This indicates that consumption of ash particles by individual chickens leads to substantial raise in their eggs toxicity.

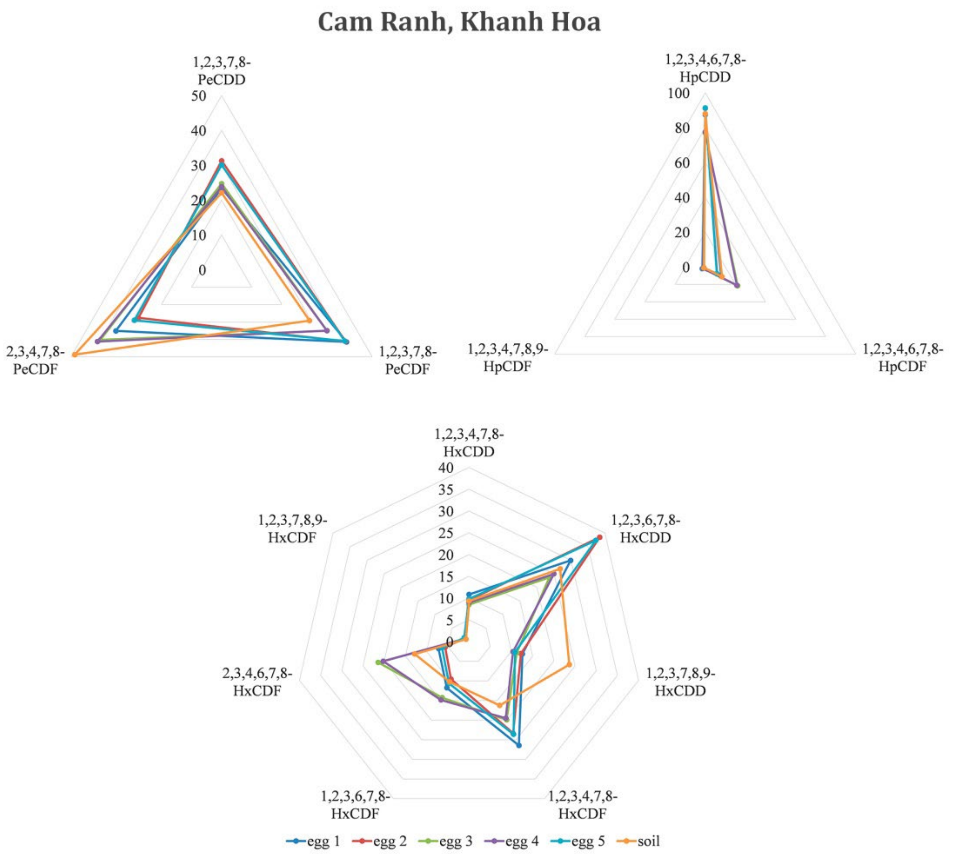

Figure 4. PeCDD/F, HxCDD/f and HpCDD/F profiles in individual free-range chicken eggs and soil from household in Cam Ranh, Khanh Hoa province.

Overall, analyzing profiles of separate homologue classes provided a good enough match between soil and egg in eggs apart from soil, mainly ash from open burning of household waste, in several households where a clear mismatch is present. Common practice of domestic waste combustion in the yards available for foraging chickens may lead to unacceptable levels of eggs contamination.

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