

EU-WIDE ENVIRONMENTAL AND EXPOSURE MONITORING OF DIOXINS, PCBS AND OTHER PERSISTENT ORGANIC POLLUTANTS (POPS) IN BUTTER AND CORRELATIONS TO PUBLISHED AIR DATA

Umlauf G, Mariani G, Amalfitano L, Vives I, Mueller A, Skejo H and Weiss J

Institute for Environment and Sustainability (IES) European Commission Joint Research Centre (JRC), Via E. Fermi 2749, 21027 Ispra (VA), Italy

Introduction

Persistent Organic Pollutants that accumulate to hazardous levels in living organisms pose environmental and health risks. Among many regulatory efforts on national level their reduction or elimination worldwide is subject to multilateral environmental agreements such as the Stockholm Convention on POPs. Within the EU the "Community Strategy for Dioxins, Furans and Polychlorinated Biphenyls" sets up the objective to reduce dioxins and PCBs in the environment, animal feed and the food chain (European Commission 2001). More recently the Regulation on persistent organic pollutants entered into force (European Commission 2004), providing the basis for implementing the provisions of the Stockholm Convention. Dioxins, Furans and PCBs are listed as unintentionally released POPs for which the releases should be continuously and cost-effectively reduced as soon as possible.

Suitable indicators for POPs are needed that allow an EU wide estimation of human food chain exposure and, at the same time, reflect the contamination level of the environmental compartment from which they derive. Dairy lipids available from all geographic regions, ideally serves for this purpose for a couple of reasons:

1. It contributes up to 95% of average human exposure with dioxins and dioxin-like PCBs and many other POPs ¹. Thus, obtaining representative contamination data on the main animal fat compartments of human diet will allow creating realistic exposure scenarios on the basis of regional consumption data.
2. It reflects the level of persistent pollutants in the environmental compartments due to the well-known effects of bioaccumulation/-magnification in the lipid fraction of the organisms growing there (e.g. atmospheric pollution-deposition on plants-cow-milk fat), assuming no relevant contamination source from feed etc. Examples of transfer studies on dairy lipids are: Daily intake of a lactating cow via grazing is equivalent to an intake from breathing approximately 100 000 m³ of air ². Up to 0.66kg dioxins were estimated to be transferred annually from the atmosphere to the UK pastures ³.
3. Once calibrated against the levels of POPs in its respective compartment, the lipid may provide a cheap and commercially available monitoring matrix. The effort in data acquisition is much lower when compared to classical methods like high volume air sampling, soil sampling and water sampling, where often no appropriate infrastructure is available and where permits from local authorities are needed. This is especially needed within the global monitoring program of POPs (<http://www.chem.unep.ch/gmn/>).
4. Moreover, this biomonitor is well buffered against temporal variations and provide an extended spatial representativity when compared to classical point measurements.

The project is a pilot and is aimed at evaluating whether a robust relationship can be established between POPs in commercially available milk products when compared to analytical data on POPs in ambient air. If so, commercial dairy products with a declaration of their origin could be used for monitoring POPs levels in air where no sampling stations do exist. The content of POPs in milk fat from cattle fed with roughage is closely related to the levels of POPs in the ambient air where the feed grows. First trails have been conducted to use butter for estimating the spatial distribution of POPs in ambient air ⁴⁻⁶. Transfer factors for some POPs such as Dioxins are available in order to compute POP levels in feed and ambient air calculate from the POPs content of milk fat ^{7, 8}. However, these transfer factors were derived from controlled experiments. Hence it remains to be verified if and under which conditions they can be applied in the field in order to assess ambient air quality. The project aims at a calibration of the model and is conducted within EU, where air data is available and where we have sampled milk and butter.

Materials and Methods

The target compounds of this study are PCDD/Fs, dioxin like PCBs, Indicator PCBs, Polybrominated Diphenyl Ethers (PBDEs), and halogenated pesticides subject to the Stockholm Convention as by 2009. Analyses are executed with High Resolution GC/MS according to the requirements of CEN and USEPA and described elsewhere⁹. Quantifications will be carried out based on labeled surrogate standards. The analytical protocols for all analytes have been validated through successful participation to international intercalibration studies.

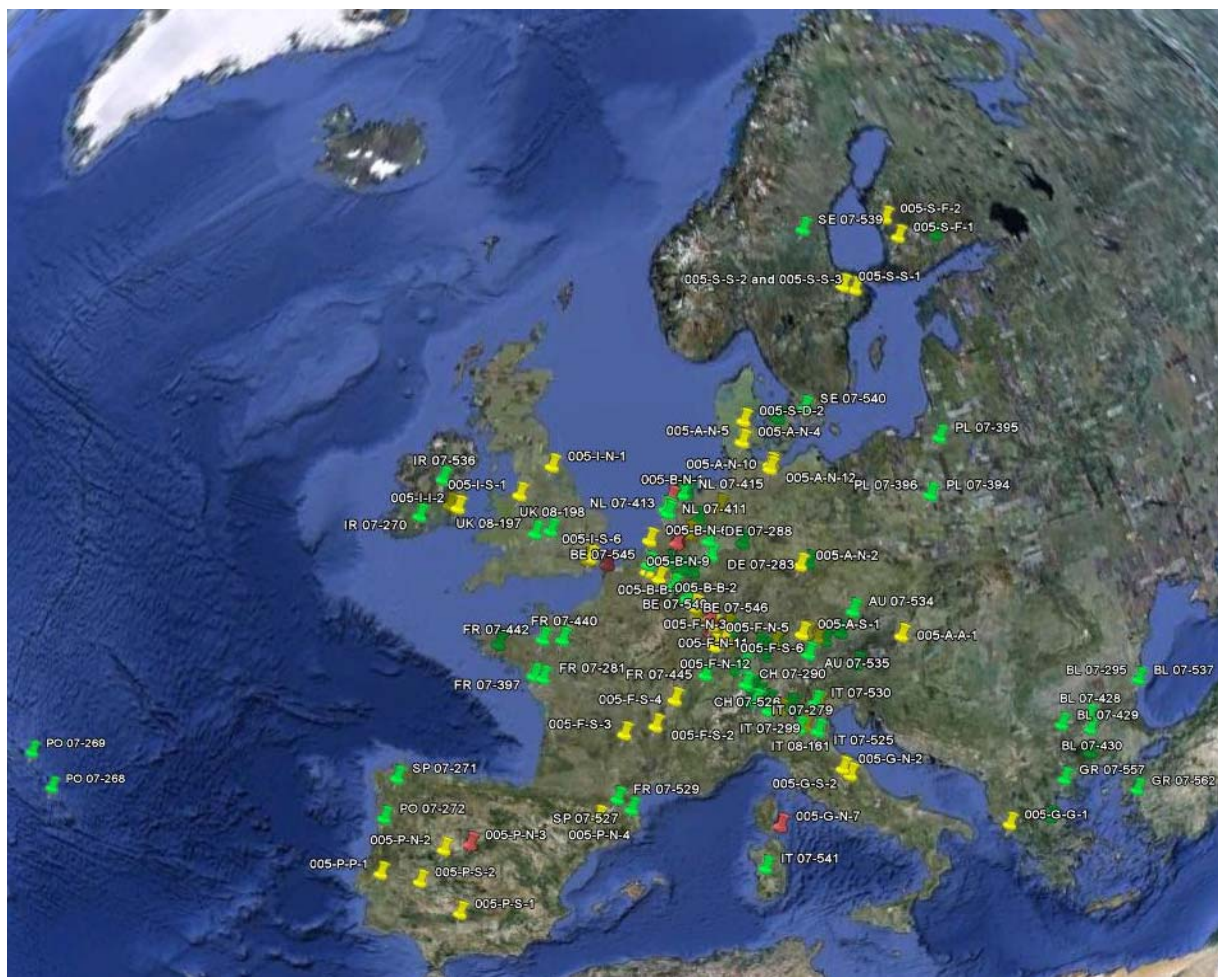


Figure 1: Sampling location of the 2001 milk survey (yellow dots) and the 2007 organic dairy products (green dots). Red dots indicate uncertain coordinates of the origin.

The experimental approach is based on 2 sets of dairy product samples:

1. The 2001 milk survey: From a sampling campaign aiming at evaluating the levels of on dioxin-like PCBs in European (EU 15) food and feedstuff, conducted by BIPRO on behalf of DG ENV in 2001 (European Commission 2001), 88 milk samples from 68 locations were selected for this study (see yellow marks in Figure 1). All samples were taken directly from farms to have control over the coordinates of the grazing cows.
2. The 2007 organic dairy product survey: While the 2001 milk survey had been executed by a contractor the 2007 survey was executed in house. Certified (European Commission 1991) organic ('Bio') farms were targeted where available, alternatively samples were collected directly from the farm. In this way the cattle had been grazing or fed

with greens from local production and consequently, that the concentration of POPs in the milk reflects the levels in ambient air. 63 butter and 22 milk samples were collected (see green marks in Figure 1).

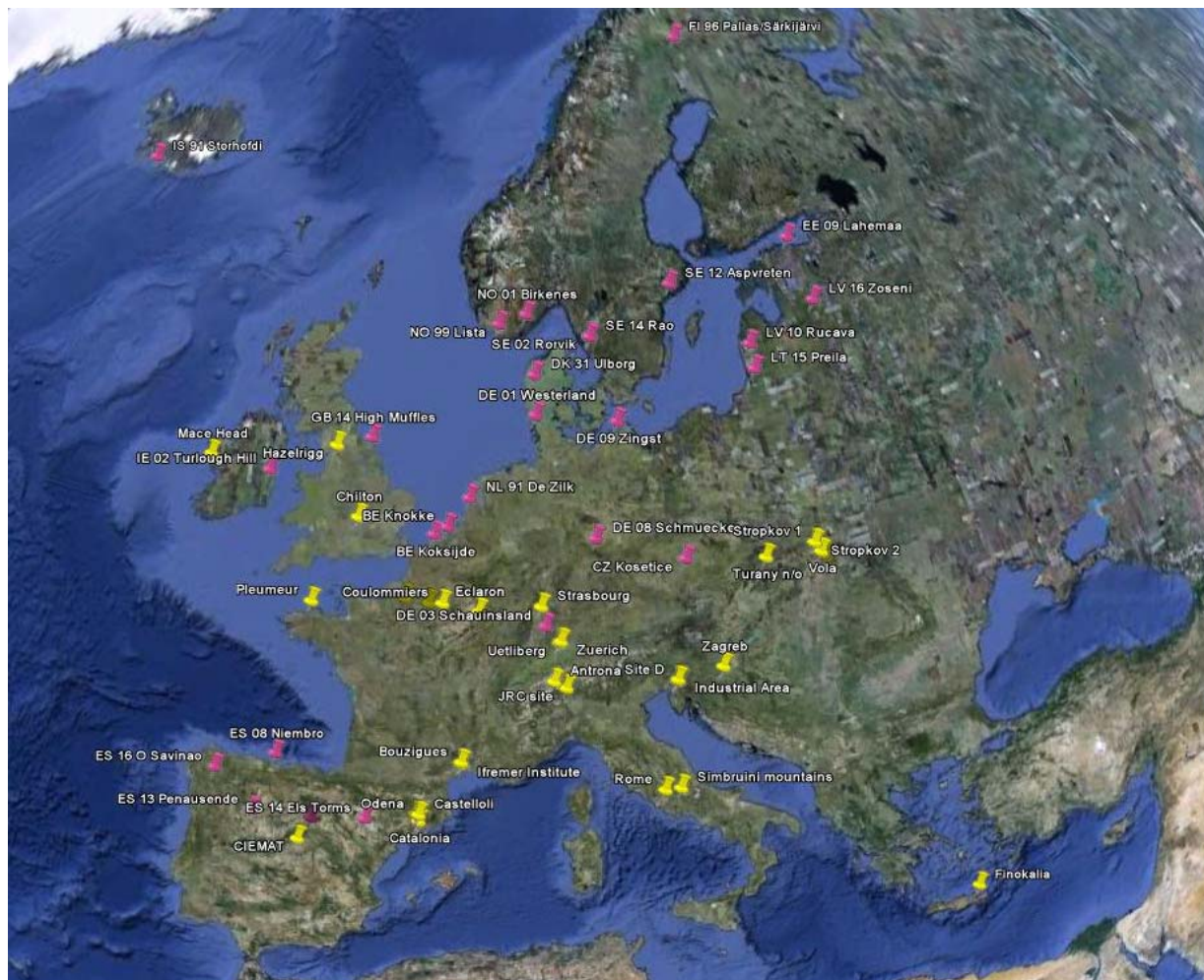


Figure 2: The location of available air data from literature (yellow dots, 1996-2007) and from the EMEP database (pink dots, 1991-2006).

Available air data, reviewed from reported studies together with JRC owned data will be correlated to concentrations in the lipid samples of the corresponding areas. One of the largest sources of seasonal, congener specific data on POPs will be retrieved from the European Monitoring and Evaluation Programme (EMEP). EMEP has the largest pan-European coverage of air levels of priority pollutants (pink marks in Figure 2), but there is a lack of data sources from the south-eastern countries which are nicely covered by literature data (yellow marks in Figure 2).

A third survey will be used to evaluate the calibrated method for regional concentrations in air based on lipid levels. For that purpose non-European samples have been gathered. It is expected that the POP profile will differ significantly between continents depending on the industrial and socio-economic situation in the country. So far samples from Brazil, Kenya, Mauritius, Morocco, Iceland and New Zealand have been stored for analysis and more samples are expected.

Results and discussion

To illustrate the intended outcome of the project we compared the air concentrations of γ -HCH reported in 2006 and modeled in EMEP to the γ -HCH levels in the milks samples from 2001 (Figure 3.). Although the air and milk levels are from different sampling years a hotspot area was identified by both approaches in the south of Belgium, close to the French border.

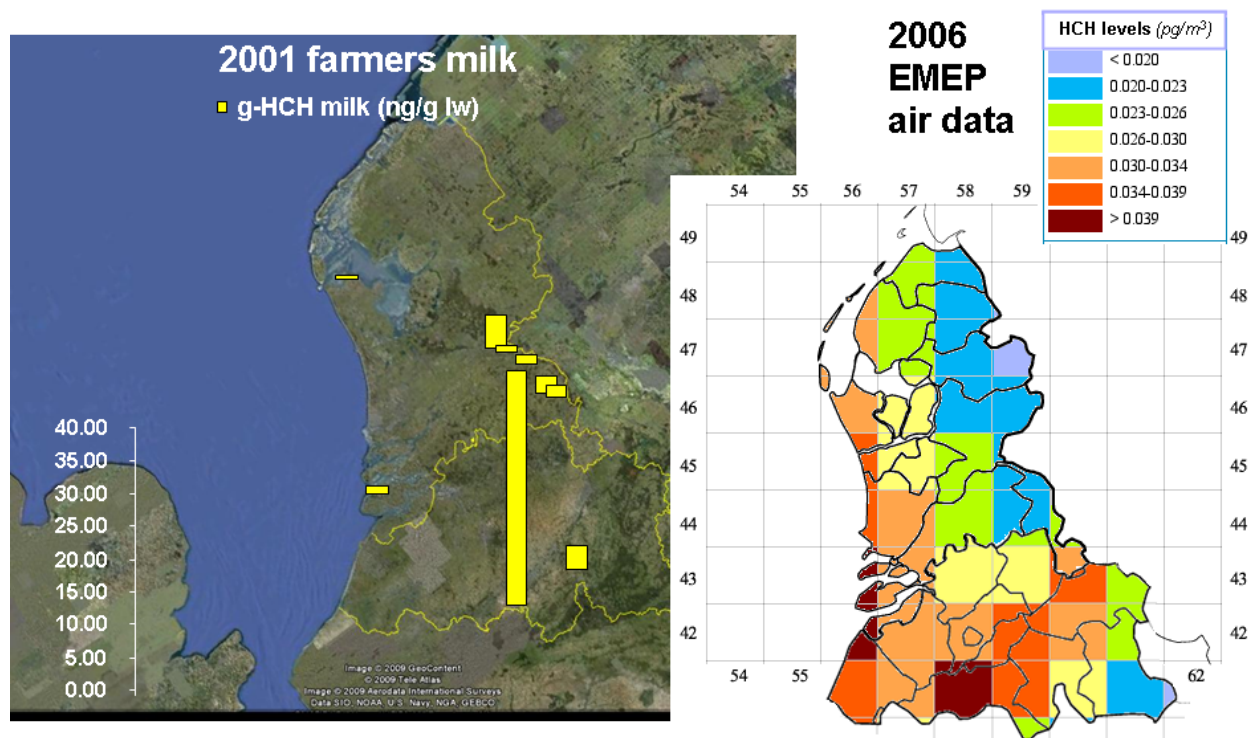


Figure 3. A comparison between air and milk levels of γ -HCH in the Benelux countries

Acknowledgement

The authors would like to acknowledge Ramon Guardans, Heidelore Fiedler and Frans Verstraete from the Global Monitoring Network for valuable input to the project.

References

1. Kelly, B. C.; Ikonomidou, M. G.; Blair, J. D.; Morin, A. E.; Gobas, F. A. P. C., (2007); *Science* 317, 236-239.
2. McLachlan, M. S., (1997); *Chemosphere* 34, (5-7), 1263-1276.
3. Thomas, G. O.; Jones, J. L.; Jones, K. C., (2002); *Environmental Science & Technology* 36, (11), 2372-2378.
4. Malisch, R.; Dilara, P., (2007); *Chemosphere* 67, (9), S79-S89.
5. Santillo, D.; Fernandes, A.; Stringer, R.; Alcock, R.; Rose, M.; White, S.; Jones, K.; Johnston, P., (2003); *Food Addit. Contam.* 20, (3), 281-290.
6. Weiss, J.; Pöpke, O.; Bergman, Å., (2005); *Ambio* 34, (8), 589-597.
7. Leeman, W. R.; Van den Berg, K. J.; Houben, G. F., (2007); *Food Addit. Contam.* 24, (1), 1-13.
8. Lorber, M.; Pinsky, P., (2000); *Chemosphere* 41, 931-941.
9. Mariani, G.; Amalfitano, L.; Manni, A.; Müller, A.; Skejo, H.; Umlauf, G. 2009; *Dioxin2009*, Beijing, China, Beijing, China, 2009; pp 2796-2801.