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Spatial distribution of Lindane concentration in topsoil across France

T.G. Orton [a,*], N.P.A. Saby [a], D. Arrouays [a], C.C. Jolivet [a], E.J. Villanneau [a], B.P. Marchant [b,1], G. Caria [c], E. Barriuso [d], A. Bispo [e], O. Briand [f]

[a] INRA, US 1106 InfoSol, F-4075 Orléans, France
[b] Rothamsted Research, Harpenden, Hertfordshire AL5 2JQ, UK
[c] INRA, US0010 Laboratoire d'Analyse des sols, 273 rue de Cambrai 62000 Arras, France
[d] INRA, AgroParisTech, UMR1091, Environnement et Grandes Cultures, 78850 Thiverval Grignon, France
[e] ADEME Waste and Soil Research Department, 20 Avenue du Grésillé, BP 90406, 49004 Angers Cedex 01, France
[f] ANSES, Laboratory for Food Safety, 23 Avenue du Général de Gaulle, 94706 Maisons-Alfort Cedex, France

HIGHLIGHTS

► Lindane concentrations in France are largest in agricultural soils.
► This demonstrates its ability to persist in the environment.
► Lindane concentrations in soils across France are larger in areas of greater rainfall.
► This is probably due to volatilization, atmospheric transport, and re-deposition.
► Maps show larger Lindane concentrations in north and northwest France (areas of more intense cropland).

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ABSTRACT

Lindane [γ-hexachlorocyclohexane (γ-HCH)] is an organochlorine pesticide with toxic effects on humans. It is bioaccumulative and can remain in soils for long periods, and although its use for crop spraying was banned in France in 1998, it is possible that residues from before this time remain in the soil. The RMQS soil monitoring network consists of soil samples from 2200 sites on a 16 km regular grid across France, collected between 2002 and 2009. We use 726 measurements of the Lindane concentration in these samples to (i) investigate the main explanatory factors for its spatial distribution across France, and (ii) map this distribution. Geostatistics provides an appropriate framework to analyze our spatial dataset, though two issues regarding the data are worth special consideration: first, the harmonization of two subsets of the data (which were analyzed using different measurement processes), and second, the large proportion of data from one of these subsets that fell below a limit of quantification. We deal with these issues using recent methodological developments in geostatistics. Results demonstrate the importance of land use and rainfall for explaining part of the variability of Lindane across France: land use due to the past direct input of Lindane on cropland and its subsequent persistence in the soil, and rainfall due to the re-deposition of volatilized Lindane. Maps show the concentrations to be generally largest in the north and northwest of France, areas of more intensive agricultural land. We also compare levels to some contamination thresholds taken from the literature, and present maps showing the probability of Lindane concentrations exceeding these thresholds across France. These maps could be used as guidelines for deciding which areas require further sampling before some possible remediation strategy could be applied.

1. Introduction

Lindane [γ-hexachlorocyclohexane (γ-HCH)] is an organochlorine pesticide (OCP) that is bioaccumulative and can remain in soils for long periods (Martijn et al., 1993; Manz et al., 2001; Nawab et al., 2003). It has harmful toxic effects on humans (Willett et al., 1998), and is defined as a persistent organic pollutant (POP). In the past, it has had various usages, including as treatments for lice and scabies in humans and for mange in domestic animals. In particular, France was a major source of Lindane in Europe (Prevedouros et al., 2004), where it was used as a broad-spectrum insecticide for soils (under corn or beet; INRS, 1992), as a treatment for a large number of crops, trees, vegetables, and seeds (for cereals, colza, and flax). Lindane is still currently included in the constitution of more than 500 commercial products including antiparasites, pharmaceutical and agricultural products (Fabre et al., 2005). In France, it was banned

* Corresponding author.
E-mail address: Thomas.Orton@derm.qld.gov.au (T.G. Orton).
[1] Present address: British Geological Survey, Keyworth, Nottingham NG12 5GG, UK.

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as a wood preservative in 1993, and for agricultural uses according to the legislative decree 92-1074 of October 2nd, 1992. However, Lindane was truly banned for agricultural uses only from July 1st, 1998, by the commission of antiparasites products for agricultural uses, after signing of the Arrhus protocol by France on June 24th, 1998. However, due to its potential to persist in soils, it is possible that traces will be found in the soils of France today.

If possible remediation strategies are to be considered (in the event of areas of Lindane contamination), then it is important to 1. understand the major factors that dictate the spatial distribution of Lindane in soils, and 2. map this distribution as accurately as possible. In order to achieve these goals in France, soil samples have been collected on a 16 km × 16 km grid across the entire French territory; this constitutes the RMQS database ("Réseau de Mesures de la Qualité des Sols", Arrouays et al., 2002). In a first phase of this project, 105 samples from the north and 78 from an east-to-west transect across the width of France were analyzed for their Lindane concentrations. Villanneau et al. (2009) presented results from this first phase (in which they found Lindane to be present in all soil samples and suggested that the source may have been volatilized Lindane that was transported by prevailing winds and deposited by rainfall in a densely inhabited depression). In a second phase of the project, 495 of the samples from the remainder of France were measured for their Lindane concentrations (not all, due to financial constraints). In the current study, we analyze the data from the two phases together, to understand and map the spatial distribution of Lindane across the entirety of France.

Several factors are known to influence the distribution of Lindane in soil. Locations close to potential Lindane sources will likely have larger concentrations than those further away (e.g. Gong et al., 2004; Li et al., 2006; Cheng et al., 2008). However, large concentrations have also been observed at locations far away from sources (e.g. in the Arctic, Fellin et al., 1996; Li et al., 1998), demonstrating the potential for its transport over long distances and its re-deposition into the soil. When in the soil, Lindane can remain there for long periods, depending on the soil type, land use, organic carbon content and other environmental factors (e.g. climate) governing its breakdown rate (Hitch and Day, 1992; Smith et al., 1993; Cousins et al., 1999; Phillips et al., 2005; Škrbić and Durišić-Mladenović, 2007). The importance of each of these factors can differ with the scale of study. For instance, a field-scale study would not be able to demonstrate any effects of land use on Lindane concentrations, whereas this might be possible in a regional-scale study. Similarly, at a regional scale, we may not see any effects of climate that may be demonstrable at a national scale. The current study offers the opportunity of investigating explanatory factors at a national scale and thereby assessing the impact of factors, such as climate, that vary over this scale.

Geostatistics provides an appropriate set of methods for analyzing spatial datasets such as ours (Webster and Oliver, 2007). In particular, the geostatistical linear mixed model (LMM; Stein, 1999) allows us to test for evidence that the potential explanatory factors contain useful information for describing our data. Subsequently, with the explanatory factors chosen, we can use the LMM to calculate predictions at unsampled locations, and thereby build a map of the Lindane concentration across France. The Lindane dataset presents two important statistical issues, which mean that commonplace geostatistical practice cannot be routinely applied to analyze the data. We must deal with these issues if we are to obtain reliable statistical results. First, the samples were analyzed for their Lindane concentrations in two phases, each phase using a different measurement procedure. Although Villanneau et al. (2009) analyzed data from the first phase, the harmonization of the data from the two phases presents a new challenge in this work. Baume et al. (2011) presents an approach for harmonization of datasets from different countries with different measurement protocols. The approach consists of adding different bias corrections to the data from each different phase (or network), and we deal with the harmonization issue using similar ideas here. Second, a considerable percentage of the data (53%) from the second phase of analysis fell below a limit of quantification, meaning that their concentrations could not be determined to a sufficient degree of precision. We apply a censored data approach to deal with this issue (e.g. De Oliveira, 2005; Fridley and Dixon, 2007), following the methodology set out in Orton et al. (2012).

We describe the study area and data, and present some candidate covariates with potential for explaining the spatial distribution of Lindane concentration across France. We then present some details of the particular geostatistical methodology that we subsequently apply to test measurement error models, harmonize the data from the two phases, and select the best set of covariates to explain and map Lindane. We discuss the results, in terms of the benefits of considering the particular statistical methodology considered here, and in terms of the spatial distribution and its explanatory factors across France.

2. Lindane data

2.1. The French national soil monitoring network: RMQS

The RMQS database ("Réseau de Mesures de la Qualité des Sols", Arrouays et al., 2002) consists of observations of soil properties on a 16 km regular grid across the 550,000 km^2 French metropolitan territory (mainland and Corsica): here we consider just data from the mainland. In total, 2200 sites were sampled, starting in 2002 with completion in 2009. If possible, sites were selected at the center of each 16 km × 16 km cell; otherwise (e.g. in urban areas, in rivers and on roads), an alternative cultivated or undisturbed location was selected as nearby as possible within a 1-km radius. When this was not possible the cell was omitted. The RMQS network was designed to monitor soil properties and in particular to identify diffuse contamination either due to atmospheric deposition of trace elements on soils or to agricultural practices (e.g. fertilizers, sludge amendments, and inorganic pesticides). Indeed, several studies have used data from the RMQS network to study variability of trace elements (Saby et al., 2009; Marchant et al., 2010), POPs (Villanneau et al., 2011), soil carbon (Martin et al., 2011; Meersmans et al., 2012a, 2012b), and various other soil properties (Arrouays et al., 2011) across France.

At each site, 25 individual core samples were taken of the topsoil (0–30 cm) layer, using an unaligned sampling design within a 20 m × 20 m area. The 0–30 cm layer was chosen to ensure consistency with existing surveys and because in France 30 cm is the maximum depth at which topsoil is affected by plowing. Core samples were bulked to obtain a composite sample for each site. Soil samples were air-dried and sieved to pass 2 mm before analysis (French standard; NF-ISO-11464, 2006).

2.2. Soil sample analyses

Analysis of soil samples for their Lindane concentrations was undertaken in two phases. During the first phase (Phase A), samples were analyzed from 105 locations in the north of France and 78 following an east-to-west transect across the width of the country; in phase A, the sample from every grid cell was measured. In the second phase of measurement (Phase B), the samples from 495 locations covering the remainder of France were analyzed; in phase B, every other grid cell was used (i.e. giving data on a 32 km × 32 km grid from this second subset). This gave data for a total of 678 sites from mainland France, as shown in Fig. 1. All maps in this paper were produced using the freely available software, Generic Mapping Tools (Wessel and Smith, 1991).

The phase A samples were analyzed using Pressure Liquid Extraction, adsorbent for purification, and gas chromatography coupled with electron capture detector for compounds separation and measurement. Phase B samples were analyzed using Head Space/Solid Phase Micro Extraction modules for extraction and purification,