Water Air Soil Pollut (2007) 186:311–321
DOI 10.1007/s11270-007-9487-9

# Factors Controlling the Spatial Variability of Copper in Topsoils of the Northeastern Region of the Iberian Peninsula, Spain

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Received: 22 January 2007 / Accepted: 5 August 2007 / Published online: 6 September 2007

**Abstract** The sources of copper topsoil variability in agricultural have been evaluated in the northeastern region of the Iberian Peninsula (Spain) using 624 soil samples collected in a standard 8×8 km grid. Analyses of variance combined with geostatistical methods have been used to map the spatial variability and to evaluate the relative contribution of natural and anthropic copper sources in topsoils. The use of the residual values derived from the interpolation method have led to the identification of local anomalies in the copper content in relation to agricultural practices carried out on the land. Copper concentrations were relatively low (17.33±14.97 mg/kg) in areas with a high pH level (>8.2) and low organic matter (<1%). In general, the spatial distribution of copper showed a good relationship with the surface evidence of the lithologic units at a regional scale. At a smaller scale, concentration values also indicated the anthropogenic influence related to specific agricultural practices in relation to land use and cultivation methods. The highest mean concentrations were found in vineyards and olive fields. These were partly due to inputs from inorganic fertilisers, mainly copper sulphate, and also to the application of liquid and soil manure.

**Keywords** Copper topsoil · Spatial variability · Iberian Peninsula

## 1 Introduction

The natural concentration of heavy metals in arable soil depends primarily on the parent material composition (Nan et al. 2002; De Temmerman et al. 2003). However, agricultural practices generally cause an enrichment of these elements (Kashem and Singh 2001; Mantovi et al. 2003). In such a land use environment, the contribution of metals from anthropogenic sources in soils can be higher than the contribution of those of a lithologic type (Liu et al. 2005).

A large proportion of toxic concentrations of trace metals (e.g., copper, among others) is introduced from cultivation methods, such as organic and mineral fertilisation, the application of pesticides, irrigation water, etc. (Romic and Romic 2003). Heavy metals can also reach the soil through the application of liquid and solid manure, such as compost or sludge, in which some metals can be particularly concentrated (Webber 1981). Specifically, copper and zinc are present in some manure in amounts which could significantly contribute to their concentration in soils (Mantovi et al. 2003). The application of contaminated organic waste is also considered an important source of heavy metals in the environment (Tichy et

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al. 1997). Applying cow manure increases the redox potential and a consequential increase in the soil solution concentration of iron, manganese and phosphorus that may influence availability of other heavy metals (Kashem and Singh 2001). Breslin (1999) showed that compost may elevate the concentration of metals, including copper. Sewage sludges disposed on land often contain considerable amounts of Cu that present a permanent risk not only for crops, but also for animal or human physiological functions through the food chain (Nan et al. 2002). Atanassova (1999) showed that more than 70% of copper is specifically adsorbed by soil.

The problems associated with the characterisation of heavy metals in most of the cultivated areas are often due to the multiplicity of pollution sources (Serrano et al. 1984; Hanesch et al. 2001), interaction with the parent material and the diversity of the type of heavy metal. Moreover, variation at some scales may be much greater than on others (Yemefack et al. 2005). In the study area, previous works showed that in topsoil, copper is the heavy metal whose concentration is more dependent on agricultural practices (Rodríguez Martín et al. 2006).

Our hypothesis is that it is possible to use the residual values of the spatial interpolation derived from geostatistical methods to evaluate the relative role of the two factors considered in this work: lithologic classes and agricultural practices (cropping lands). Geostatistics provides a set of statistical tools for incorporating the spatial component in data processing. This allows for the description and modelling of spatial patterns, predictions at unsampled locations, and an assessment of the uncertainty attached to these predictions (Goovaerts 1998). In order to unravel the effects of the two factors in current spatial variability of topsoil copper content, a system analysis can be performed in two steps. The first step consists of a spatially explicit analysis of the regional distribution of copper that could be related to the lithologic units given that this factor is more significant at large spatial scales. The second step involves the analysis of kriging residuals as a random component once the spatial variability that attributed to the lithologic factor has been removed. The second analysis is focused on clarifying the effects at smaller scales that are mainly related to agricultural practices.

The primary objective of this study was to analyse the spatial distribution of topsoil copper concentration by means of geostatistical methods in order to evaluate the contribution of the two main factors involved: lithologic classes and agricultural practices (cropping).

## 2 Materials and Methods

### 2.1 The Study Area

The study area, located in the north-eastern region of the Iberian Peninsula, has three mountain ranges: the Pyrenees in the north, the Iberian Chain in the southwest, and the Catalonian Coastal Ranges in the southeast. Agriculture is important in the region of the Ebro River, and agricultural practices extend over 4.2 million hectares (Fig. 1) of agricultural land in the Ebro basin (total area basin, 9.5 million hectares). Cereals represent the largest proportion of this cultivated area (53.4%). Fruit production and vineyards (7.7% and 6.0%, respectively) are also important in the area. The Ebro River zone, with a population of around 3.25 million, is intensively industrialised. This human activity generates an environmental impact that can have negative repercussions on soils and negative effects on the quality of agricultural products (Gil et al. 2004). In general, soils in the terraces and the flood bed of the river Ebro are rich and apt for agriculture, and they collectively cover more than 30% of the surface area in the Ebro depression. Although the heterogeneity of these soils predominates, the sharp slopes mean that the rock is exposed and the extreme aridity of the region leads to skeletal soils in the southeast and in areas of the Ebro valley.

Most of the exposed rocks within the basin area are of the Oligocene–Miocene age (including clastic, evaporite and carbonate facies) and are of alluvial and lacustrine origins. They were deposited during an endorheic period of the evolution of the basin (Riba et al. 1983; Simon-Gomez 1989). During the Quaternary, incision of the drainage system caused the isolation of structural platforms, the tops of which are composed of near-horizontal Neogene limestones. In the recent past, several nested levels of alluvial terraces and pediments were developed, and their deposits overlay the Neogene gypsum and marls (Simón and Soriano 1986). The Quaternary levels comprise mainly gravels, sand and slits.

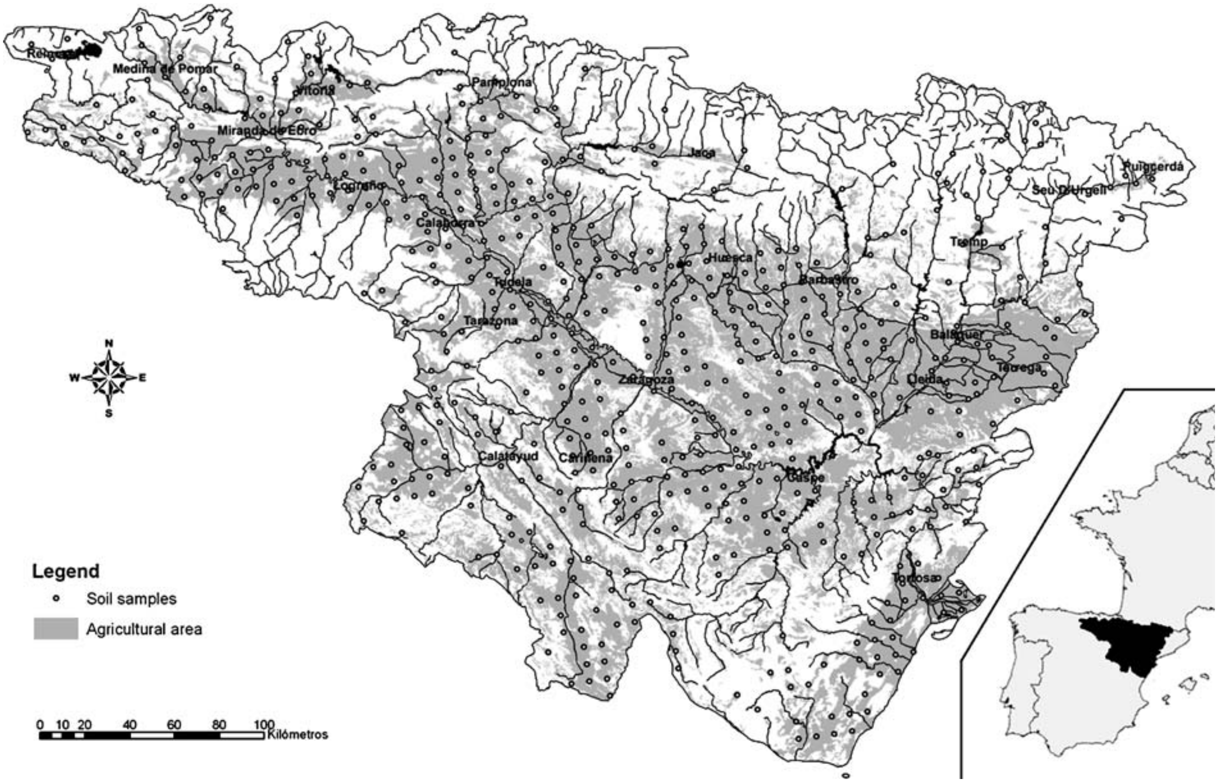

Fig. 1 General map of 8×8 km, showing the 624 samples on agricultural area

### 2.2 Soil Samples

The sampling scheme was a 8×8 km grid nested within the 16×16 km grid designed in the European ICP-Forest programme (Montoya Moreno and Lopez Arias 1997). Sampling points on each land use type were selected using aerial photos (orthophoto with 1 m spatial resolution). In each selected node of the grid, a representative sample was composed of 21 subsamples at 10 m apart from each other on a hexagonal pattern. Soil samples were collected from the upper 25 cm of soil depth, using the Eijkelkamp soil sampling kit. Further details relating to sampling can be found in López-Arias and Rodríguez (2005). A total of 624 locations were sampled from 2003 and 2004.

### 2.3 Analytical Methods

Soil samples were air-dried and sieved at 2 mm. Three fractions (sand, silt, clay) of soil texture were determined for each sample using the pipette method. After shaking with a dispersing agent, the sand (2 mm–63 μm) was separated from the clay and silt with a 63 μm sieve (wet sieving). The clay (<2 μm) and silt (63–2 μm) fractions were determined by the pipette method (sedimentation). Standard soil analyses were carried out to determine the soil reaction (pH) in a 1:2.5 soil–water suspension (measured by a glass electrode CRISON model Microph 2002) and organic carbon by dry combustion (LECO mod. HCN-600) after ignition at 1,050°C and discounting the carbon contained in carbonates. Carbonate concentration was analysed by a manometric measurement of the $CO_2$ released following acid (HCl) dissolution (Houba et al. 1995).

Copper content was extracted by aqua regia digestion ($HNO_3$, HCl and $H_2O_2$) of the soil sample in a microwave (Milestone Ethos 900 plus Mod. 44062) in accordance with the ISO 11466 procedure (International Organization for Standardization 1995). Copper in soil extracts was determined by optical emission spectrometry (IPC) with a plasma spectrometer ICAP – AES IRIS ADVANTAGE DUO ERS DV Model 14034100 of Thermo Optek. The accuracy of the method was verified by analysing a calcareous loam soil, CRM 141 R standard reference material (Quevauviller et al. 1996).

## 2.4 Statistical Analyses

All statistical analyses were carried out using the statistical package SPSS v11, GS+ v5 and the Geostatistical Analyst (Johnston et al. 2001) extension for ArcGis 8.3. The values were transformed (logarithmically) and the new values were generally closer to a normal distribution. Two-way analyses of variance (ANOVA) were utilised to determine which of the two main factors (lithology and cropping lands) had a statistically more significant effect on the topsoil copper content. These statistical analyses, however, ignore the spatial component which includes important information on Cu concentration (Lin 2002). We thus performed a second two-way ANOVA after the geostatistical analyses and kriging process, incorporating the spatial component as a covariable.

### *2.4.1 Variogram Analysis*

Geostatistics is based on experimental variograms which provide a means of quantifying the relationship between the values of the samples and the distance between pairs of samples (Lin 2002). The semivariance in the variogram $\gamma$ is calculated using the relative locations of the samples (Goovaerts 1998). In this study, the variogram type and initial parameters were selected after several tests. Spherical models were fitted to the experimental semivariogram using a least-squares fit to the experimental variogram, with empirical weighting being proportional to the number of point pairs and inversely proportional to the square of the estimated semivariance of each (Cressie 1991). This emphasises the reliable estimation of nugget and close-range behaviour, to which interpolation is most sensitive (Yemefack et al. 2005).

### *2.4.2 Kriging Mapping*

The main application of geostatistics to soil science has been the estimation and mapping of soil attributes in unsampled areas (Goovaerts 1998; Liu et al. 2004). Prediction is made possible by the existence of spatial dependence between observations as assessed by the correlogram or semivariogram. Kriging is a linear interpolation technique that provides the best linear unbiased estimate for spatial variables. Kriging estimates are calculated as weighted sums of the adjacent sampled concentrations. That is, if data appears to be highly continuous in space, the values nearer to those estimated receive higher weights than those that are farther away (Ersoy et al. 2004). The soil copper content was mapped by ordinary kriging (OK) based on parameters derived from the spherical model of the copper variogram influence. There are many different kriging algorithms and most of them are reviewed in Goovaerts (1999) with references to soil applications. Textbooks (Cressie 1991; Goovaerts 1997) and papers (Goovaerts 1998; Juang et al. 2004) have further detailed geostatistical methods.

### *2.4.3 Analysis of Kriging Residuals; Random Component*

The estimated standard errors of kriged values were used to test the accuracy of the kriging result. These errors reflect the variability of topsoil copper content,

**Table 1** Summary statistical of copper concentrations of soil in topsoil (in mg/kg) and some other soil properties (*n*=624)

| | Mean | SD | Median | Min. | Max. | CV% | SE |
|---|---|---|---|---|---|---|---|
| Cu | 17.33 | 14.97 | 13.0 | 2.0 | 207 | 86.4 | 0.60 |
| PH | 8.09 | 0.539 | 8.2 | 4.9 | 9.0 | 6.7 | 0.02 |
| S.O.M. | 2.20 | 1.380 | 1.9 | 0.2 | 13.1 | 62.7 | 0.05 |
| $CaCO_3$ | 29.67 | 16.08 | 31.0 | 0.0 | 79.0 | 54.2 | 0.64 |
| Sand | 38.62 | 17.09 | 37.9 | 3.9 | 96.1 | 44.3 | 0.68 |
| Clay | 21.97 | 8.70 | 20.8 | 1.7 | 62.3 | 33.2 | 0.52 |
| Silt | 39.36 | 13.08 | 39.6 | 2.0 | 89.3 | 39.6 | 0.35 |

*S.O.M* Soil organic matter, *$CaCO_3$* carbonates, *SD* standard deviation, *SE* standard error, *C.V%* coefficient of variation

**Table 2** Two_ways analysis of variance for log[Cu] by land use (cropping) and lithology

| Source | Sum of squares | *df* | Mean square | *F* ratio | *P* value | Contribution % |
|---|---|---|---|---|---|---|
| Lithology | 4.79647 | 10 | 0.479647 | 8.13 | 0.0000 | 13.48 |
| Crop | 2.76047 | 10 | 0.276047 | 4.68 | 0.0000 | 7.76 |
| Error | 35.579 | 603 | 0.059003 | | | |
| Total | 43.1359 | 623 | | | | |

as indicated by the standard deviation of the original data, as well as the uncertainty inherent in interpolating from a widely dispersed site (Guo et al. 2001). The ordinary kriging estimator is exact and the kriging variance is zero at data locations (Goovaerts 1999). In the determination of errors, one point is omitted and its value is estimated based on the remaining values. Afterwards the kriged value is compared with the real value of the omitted point. This procedure is repeated for all values. The accuracy of the kriged results is acceptable if the mean of the estimated errors is less than their corresponding standard deviations. These residuals were also used as a covariable in the second ANOVA. This random component, the residuals of the kriging analyses, is a new independent variable that could provide information on the lower scale variation of Cu concentration.

## 3 Results and Discussion

### 3.1 Soil Properties and Copper Content

High pH and low organic matter content are the two typical characteristics which define the general make-up of Spanish Mediterranean soils. Soils of the area are predominately basic (the pH of 50% of samples is >8.2), due to the high percentage of carbonate in the parent materials (Table 1). The mobility and retention of metals are strongly affected by soil pH. Cations tend to be more mobile with decreasing pH levels (Martinez and Motto 2000; Kashem and Singh 2001), and more copper is adsorbed as pH levels increase. These soils were predominately used for agricultural. The average organic content was 2.20%, with values ranging between 0.2% and 13.1% (Table 1). Organic matter is the primary constituent which specifically adsorbs copper, due probably to the cation exchange capacity of organic material (Tichy et al. 1997; Martin and Kaplan 1998). The results of granulometric fractions of organic matter were, indeed, strongly related to cooper concentration (Rodríguez Martín et al. 2006). De Temmerman et al. (2003) obtained the same result for a background value of copper in northern Belgium.

Copper concentration in the area ranges between 2 and 207 mg/kg (mean, 17.3 mg/kg) in agricultural and grassland topsoils, with the highest coefficient of variation (86%). According to other authors, the normal variation of Cu in soils is between 6 and 100 mg/kg (Boluda et al. 1988) or between 5 and 50 mg/kg (Bloemen et al. 1995). In general, 60 mg/kg is the threshold value at which toxicity symptoms may occur. This critical value is exceeded in 10 plots (1.6% of samples) and only one plot higher than 200 mg/kg. These values clearly reflect anthropic activity.

A two-ways factorial ANOVA (Table 2) shows statistically significant effects of lithology and crop type on the topsoil copper content. At this stage, it is difficult to differentiate the effect of each of these factors. The highest mean concentrations (Table 3) in

**Table 3** Summary statistical of copper concentrations for lithology ($n$=624)

| Lithology | *N* | Mean | SD |
|---|---|---|---|
| Sand wares | 18 | 14.72 | 10.3 |
| Sandstone | 67 | 16.78 | 9.6 |
| Limestone | 62 | 15.58 | 8.9 |
| Armored mud balls | 41 | 14.54 | 10.3 |
| Quartzites | 10 | 23.20 | 11.0 |
| Dolostones | 8 | 13.25 | 5.7 |
| Gravels | 145 | 23.31 | 22.2 |
| Claystones | 95 | 13.87 | 9.7 |
| Marls | 56 | 12.59 | 8.3 |
| Gypsum | 46 | 22.20 | 21.2 |
| Conglomerates | 76 | 14.50 | 9.5 |
| Total Mean | 624 | 17.33 | 14.9 |

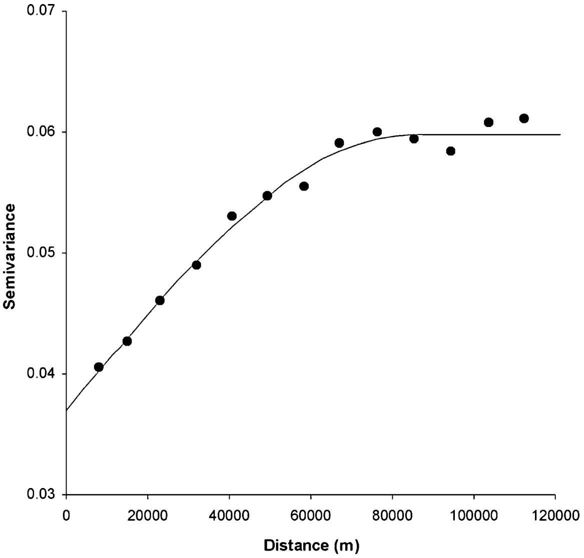

**Fig. 2** Semivariogram for Cu topsoil variation values

lithology were found on quartzites (23.2 mg/kg), gravels (23.3 mg/kg) and gypsums (22.2 mg/kg). Copper, in fact, is a cation with a huge capacity for the chemical combination with minerals and organic components of soil. However, its ionic form precipitates easily with anions such as sulphates, carbonates and oxides (Boluda et al. 1988). The residual copper present in oxides and other minerals usually constitutes around 50% of total copper. The hydrous oxides of Fe and Mn provide the main control on Cu fixation in soil (Davies 1997). The availability of metals to plants and ecosystems depends on the nature of the parent rock and the ease of weathering. Brümelis et al. (2002) and Davies (1997) in Latvia and in Great Britain, respectively, explained that soil copper content arises from pedogenesis. In this study however, this metal also indicated the anthropogenic influence related to a specific agricultural practice, particularity at a smaller scale, as evidenced here below in Section 3.2.2.

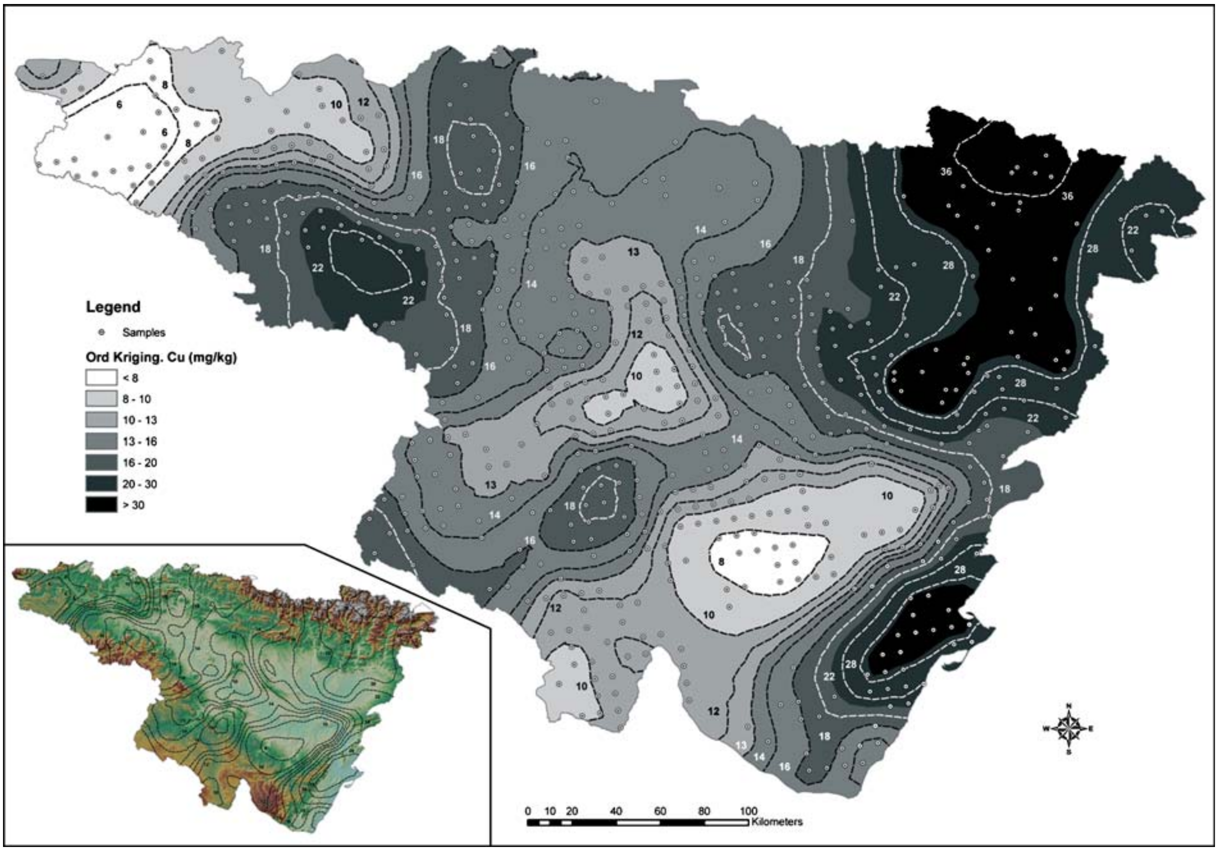

**Fig. 3** Kriging map of copper

## 3.2 Geostatistical Analysis and Copper Mapping

### 3.2.1 Description of Spatial Patterns and Semivariogram Modelling

In the geostatistical literature, spatial patterns are usually described in terms of dissimilarity between observations depending on the separation distance. Figure 2 shows the experimental semivariogram of copper measured values in agricultural land for a maximum distance of up to 120 km. No directional trend was observed and an isotropic model was fitted to the experimental variogram. Based on this semiovariogram, we can state that most of the variability is found at distances of less than 80 km.

The nugget effect ($C_0$=0.037) represents the undetectable experimental error and/or field variation within the minimum sampling spacing (Guo et al. 2001). The sill value ($C$=0.060) represents total spatial variation (Guo et al. 2001; Ersoy et al. 2004). The range ($A_0$=85 km) is considered as the distance beyond which observations are not spatially dependent (Gallardo 2003; Sun et al. 2003). The nugget/sill ratio (62%) can be regarded as a criterion to classify the spatial dependence of soil properties. If the ratio is less than 25%, the variable has a strong spatial dependence; if between 25 and 75%, then the variable has moderate spatial dependence; anything over 75% indicates that the variable shows only weak spatial dependence (Guo et al. 2001; Sun et al. 2003; Liu et al. 2004). As mentioned above, the spatial variability of copper may be affected by both intrinsic (soil parent materials) and extrinsic aspects (specific agricultural practices). Usually, a strong spatial dependence of soil properties can be attributed to intrinsic properties whereas a weak spatial dependence can be attributed to extrinsic aspects (Liu et al. 2004).

The kriging map derived from the spherical model with a 500 m spatial resolution (Fig. 3), shows areas

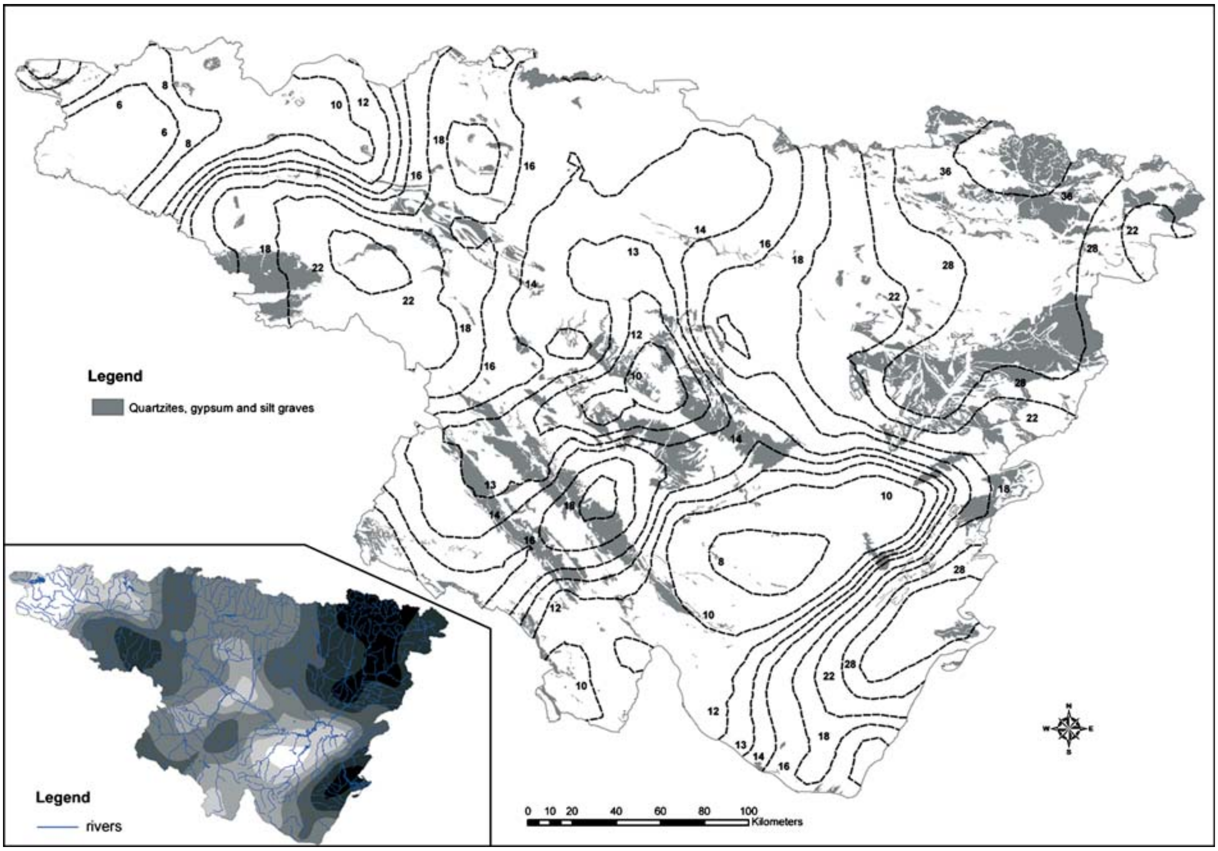

**Fig. 4** Contour map of copper concentrations in topsoil. The *shaded areas* map show quartzites, gypsum and silt gravels

**Table 4** Summary statistical of copper measurement, estimate and the difference for croplands ($n$=624)

| Crops | N | Measurement copper | | Estimate copper | | Remainder copper | |
|---|---|---|---|---|---|---|---|
| | | Mean | SD | Mean | SD | Mean | SD |
| Cereal | 306 | 15.57 | 12.36 | 15.53 | 5.07 | 0.04 | 10.86 |
| Citrus | 8 | 21.25 | 14.86 | 22.85 | 5.23 | −1.60 | 14.75 |
| Fodder farming | 91 | 14.29 | 7.89 | 13.77 | 5.16 | 0.52 | 6.54 |
| Industrial crops | 13 | 15.15 | 5.57 | 13.55 | 4.07 | 1.60 | 5.35 |
| Arable land | 30 | 13.50 | 5.32 | 14.36 | 1.83 | −0.86 | 5.22 |
| Fruit | 44 | 19.30 | 16.85 | 15.49 | 4.77 | 3.81 | 15.70 |
| Vegetable garden | 9 | 16.33 | 6.95 | 12.98 | 3.10 | 3.35 | 5.51 |
| Olive | 33 | 25.15 | 18.20 | 17.45 | 6.51 | 7.71 | 14.75 |
| Grassland | 49 | 27.04 | 30.32 | 18.79 | 9.72 | 8.26 | 28.76 |
| Tuber | 4 | 8.75 | 4.65 | 9.04 | 5.61 | −0.29 | 4.00 |
| Vineyard | 37 | 23.41 | 14.12 | 15.44 | 2.25 | 7.97 | 13.51 |
| Total | 624 | 17.33 | 14.97 | 15.05 | 5.63 | 2.28 | 13.36 |

The values have been reversed logarithmic transformation (mg/kg).

*SD* Standard deviation

of high copper concentration. The accuracy of kriged results are accepted because the mean of the estimated errors was less than the standard deviation of the original data values. The interpolated map of copper distribution generally showed good correspondence with the surface evidence of the lithologic units. The areas with higher values (Fig. 4) were principally located over silt gravels (25.34 mg/kg), quartzites (21.19 mg/kg) and gypsums (19.54 mg/kg). This is in accordance with the highest values previously shown in Table 3. Another area with high concentration levels was that surrounding the Ebro delta, which has no clear correspondence with the lithology, and contains four of the ten samples that exceeded the threshold of 60 mg/kg. Point sources of copper contamination, namely uncontrolled, active or untended waste dumps all imply great contamination risks. Evidence of human influence can be seen in the Ebro delta due to the sediment accumulation over many years. The capability of sediments to record anthropogenic influences is well known (Birch et al. 2001). River sediments are particularly sensitive to the accumulation of pollutants.

### *3.2.2 Analysis of Residuals in the Kriging Procedure*

Table 4 shows the measured and estimated values, but the difference between both by crop type, to indicate which has values that differ from those expected according to their spatial distribution. Mean differences between measured and estimate values in the kriging interpolation were higher in olive fields (7.71), vineyards (7.97), and grasslands (8.26). The difference between the measured copper value and the estimated value of a sampled point can be attributed to the distinct uses or agricultural practices, and represents the variation below the measurement scale of the grid used in the sampling. These residuals were considered as a new independent variable, increase or decrease, as compared to surrounding samples.

The results of the second ANOVA (Table 5), where the residual was taken into account as a covariable,

**Table 5** Factorial analysis of variance for log[Cu] by cropping, lithology and covariate

| Source | Sum of squares | *df* | Mean square | *F* ratio | *P* value | Contribution % |
|---|---|---|---|---|---|---|
| Covariate | 15.3415 | 1 | 15.3415 | 355.81 | 0.0000 | 59.10 |
| Lithology | 0.65506 | 10 | 0.065506 | 1.52 | 0.1283 | 2.52 |
| Crop | 1.18299 | 10 | 0.118299 | 2.74 | 0.0026 | 4.56 |
| Error | 25.9564 | 602 | 0.043117 | | | |
| Total | 43.1359 | 623 | | | | |

showed that the cropland type accounted for a greater proportion of the variance while the lithologic component was not statistically significant. These results therefore demonstrated the effect of anthropogenic components on copper concentrations in the cropping treatments. These results showed that traditional agricultural land use systems at a local level in the Ebro valley have an important effect on soil quality. Yemefack et al. (2005) showed that most soil variables were sensitive to the effects of the land use type. They also demonstrated that the contribution to total variance from the shallowest soil layer was greater than at the deepest layer for most soil variables. Copper is an essential element for plant requirements (Alloway 1995) in agriculture. The main proposes of using chemicals in agriculture are improved nutrient supply in soil (fertilisers) and disease control (pesticides), along with inorganic fertilisers (urea, calcium superphosphate, iron sulphate and copper sulphate) and pesticides (herbicides and fungicides). The yearly consumption of fertilisers in Spain is approximately $2\times10^6$ tonnes (99.3 kg/ha of the land cultivated surface) and that of pesticides in Spain is around 28,000 tonnes, which yields an average of 29.9 kg/ha of cultivated land (Gimeno-Garcia et al. 1996). The use of Cu-based pesticides and copper sulphate in conventional viticulture over the years in the Ebro basin has led to extra accumulation of Cu in topsoils. This may probably result in damage, such as that caused to vines because excessive copper availability leads to stunted root systems (Chaignon et al. 2005).

The higher copper concentration of copper in olive fields and vineyards has thus been explained by overfertilisation, although it may have a different origin in the case of grassland areas (Table 4). Anthropic copper input on grassland or cultivation lands in the Ebro basin are caused by introducing organic fertilisation (principally pig slurries). This practice is so common that it is easy to hypothesise that the major source for copper in these soils is manure application. In grassland, copper content is also favoured by a higher percentage of organic matter in soils. Agricultural effluents derived from liquid pig manure contain elevated levels of copper (Meers et al. 2005). The high copper concentrations found in the east and north-east of the centre of the Ebro valley (Fig. 3) are presumably caused by this practice. Mantovi et al. (2003) demonstrated that the copper content in pig slurries is 10-40 times higher than in liquid manure. Sewage irrigation also leads to the accumulation of copper in agricultural soils (Liu et al. 2005).

## 4 Conclusions

Variations in copper concentrations in agricultural soils of the Ebro region have both a natural and anthropic origin. The variance analysis and the geostatistical methods have been essential to determine the relative contribution of each of these two sources. The major copper variations in soils are determined by the parent material composition. The highest copper mean concentrations were found on quartzites, gravels and gypsums. Vineyards and olive fields showed the highest mean concentration of copper due to anthropic activities in the Ebro valley. However, no concentration value was considered pollutant. Copper accumulations in olive fields and vineyards may have been caused by overfertilisation. Such activities are considered to be local anomalies, and were determined in topsoil copper, which was linked to agricultural methods, particularly through the application of slurries that contain appreciable amounts of copper. The anthropogenic nature of Cu concentration also showed spatial dependence at a smaller scale.

**Acknowledgements** This study was supported by the Spanish “Ministerio de Agricultura, Pesca y Alimentación” (MAPyA) and “Ministerio de Medio Ambiente” (MMA), project CC01-0013: “Research of heavy metal contents in agricultural soils of Spain”. The authors would like to express their gratitude to the MMA and MAPyA.

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