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Concentration and Spatial Distribution of Lead in Soil Used for Ammunition Destruction

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Abstract Studies on heavy metal contamination in soils used for ammunition disposal and destruction are still emerging. The present study aimed to evaluate the contamination level and spatial distribution of lead in disposal and destruction areas. This site was used for ammunition disposal and destruction activities for 20 years. The ammunition destruction site (1,296 ha), a sampling system that followed a sampling grid (5 m × 5 m) with 30 points was adopted and samples were collected at the following five depths with a total of 150 samples. During the collection procedure, each sampling grid point was georeferenced using a topographic global positioning system. Data were validated through semivariogram and kriging models using Geostat software. The results demonstrated that the average lead value was 163 mg kg^{-1}, which was close to the investigation limit and the contamination levels were higher downstream than upstream. The results showed that there was lead contamination at the destruction site and that the contamination existed mainly at the surface layer depth. However, high lead concentrations were also found at deeper soil depths in the destruction area due to frequent detonations. According to the planimetry data, the areas that require intervention significantly decreased with increasing depths in the following order: 582.7 m^2 in the 0–20 cm layer; 194.6 m^2 in the 20–40 cm layer; 101.6 m^2 in the 40–60 cm layer; and 45.3 m^2 in the 60–80 cm layer.

Keywords Heavy metals · Extraction · Spatial variability · Geostatistics

According to the World Health Organization (WHO), 3 mg is the maximum weekly dose of lead tolerated by an adult, but blood lead levels greater than 0.8 mg L^{-1} are considered as evidence of contamination (World Health Organization 2010). Lead is mainly embedded indirectly in the environment, especially when making alloys with other metals (Brum 2010). A metal alloy composed of lead and antimony (Pb/Sb) can be used in manufacturing batteries and ammunition; as an antiknock agent in gasoline; in wood preservatives, paints, lubricating oils, toys, and pipes; and in the oil industry (Li and Wong 2006). Ammunition disposal operations in Brazil are executed by incorporating ammunition into soil, which is the only technique used for disposing explosive and ammunition residues in Brazil (Brum 2010). Moreover, lead is an integral part in virtually all primers and small caliber ammunition due to the high specific weight of lead.

While soil has a relative capacity to retain heavy metals depending on the level and frequency of ammunition disposal and destruction, this retention capacity can be exceeded resulting in contaminants being transported to surface waters, leached into groundwater, and/or introduced into the food chain. Studies that adopt geostatistical models to assess environmental contamination are

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increasingly being used (Webster 2008). Geostatistics uses variogram (or semivariogram) techniques to measure spatial variability of a regionalized variable and provides input parameters for interpolation by kriging (Webster and Oliver 2001). There are few studies, especially studies based in Brazil, of spatial variability in lead contamination in the literature. Silva et al. (2004) and McGrath et al. (2004) evaluated spatial variability in lead contamination at mining sites in Portugal and Ireland, respectively. The aforementioned studies demonstrated that the variability in lead content exhibits spatial dependence and fits spherical semivariogram models. Considering the importance of understanding and mapping spatial variability in heavy metal contamination as well as improving efficiency and reducing remediation costs, the present study aimed to assess the lead contamination level in soil at an ammunition destruction site using geostatistics as a tool.

Materials and Methods

The study area is located in the municipality of Seropédica, Rio de Janeiro state, Brazil (Fig. 1a). The study site was used for ammunition disposal and destruction activities for 20 years. Due to the need for mapping with geostatistical interpolation (ordinary kriging) at the ammunition destruction site (1,296 ha), a sampling system that followed a sampling grid (5 m × 5 m) with 30 points was adopted (Fig. 1b; points 1–30). During the collection procedure, each sampling grid point was georeferenced using a topographic global positioning system (GPS) with post-processed differential correction (DGPS; Trimble® ProXT™ model) using the UTM coordinate system, zone 23S, and horizontal datum WGS84. Samples were collected at the following five depths with a total of 150 samples: 0–20, 20–40, 40–60, 60–80 and 80–100 cm. Fifteen sampling points (five depths) were also analyzed in a circumscribed area at the ammunition destruction site, including 10 points downstream (points 31–40) and five points upstream (points 41–45) (Fig. 1b).

Surface water samples at nine points were collected as follows: one point was from a spring upstream from the destruction area (RH standard); two points were from surface water that drained downstream from the destruction area (1H and 2H); two points were from a broken dam (3H and 4H); and four points were from the drainage channel (5H the 8H). These sample collections followed the methodology recommended by technical standard 10007 (NORMA 10007) of the Brazilian Association of Technical Standards (Fig. 1b).

Geostatistical models were applied to evaluate lead spatial distribution in soil at the ammunition destruction site. The experimental variogram graph was obtained by calculating the variogram at different lags (h distance). Theoretical model fitting was performed for each experimental variogram. The following models were tested: spherical, exponential, Gaussian, and linear. The fitted model provided information about structure and input parameters for executing kriging interpolation. The kriging method was used because it is recognized as a good linear estimate without bias and uses a moving weighted average. This estimate was calculated with the following equation:

$$\hat{Z}(x_0) = \sum_{i=1}^{n} \lambda_i Z(x_i)$$

where $\hat{Z}(x_0)$is the value to be estimated at site x_0 and $Z(x_i)$ is the known value in the site sampled x_i. Weight distribution (λ_i) was not arbitrated, and its calculation was based on the parameters in the fitted variogram models. The sum of the weights is equal to one to ensure that the estimate is not biased and that the error estimate or kriging variance is minimized. From the interpolated data, Surfer 8.0 software was used to generate lead content contour maps at a resolution of 1 m.

Soil samples were air dried, sieved, homogenized, and passed through a 2.0 mm mesh sieve. Subsequently, the soil samples were digested in triplicate using block digesters with aqua regia as previously described (ISO 11466 1995). The soil extracts were read by atomic absorption spectrophotometry with a DL and QL of 0.064 and 0.15 mg L^{-1}, respectively. The detection limit (DL) of the method was calculated by the mean values from five white replications and was three times the standard deviation. Method validation was possible with the certified reference sample, NIST SRM 2709a (San Joaquin Soil, which has lead content of 17.3 ± 0.1 mg kg^{-1}). The method obtained 92 % recovery.

The surface water samples were conditioned by initially acidifying them by adding three drops of concentrated HNO_3 per liter of solution followed by filtration through a 0.45 μm filter. Lead concentrations were quantified using inductively coupled plasma optical emission spectrometry (ICP-OES; Perkin Elmer Optima 3000) and compared with the guiding values for potable and effluent discharge standards according to resolution 357 of the Brazilian National Environmental Council (CONAMA 2005).

Results and Discussion

Resolution 420 of CONAMA (2009) established guiding values for soil contaminants. For the investigation limit, the agricultural scenario/area of maximum protection was considered. Therefore, lead contamination assessment was based on CONAMA standards that use reference values for quality, prevention, and investigation limits of 17, 72 and 180 mg kg^{-1}, respectively.

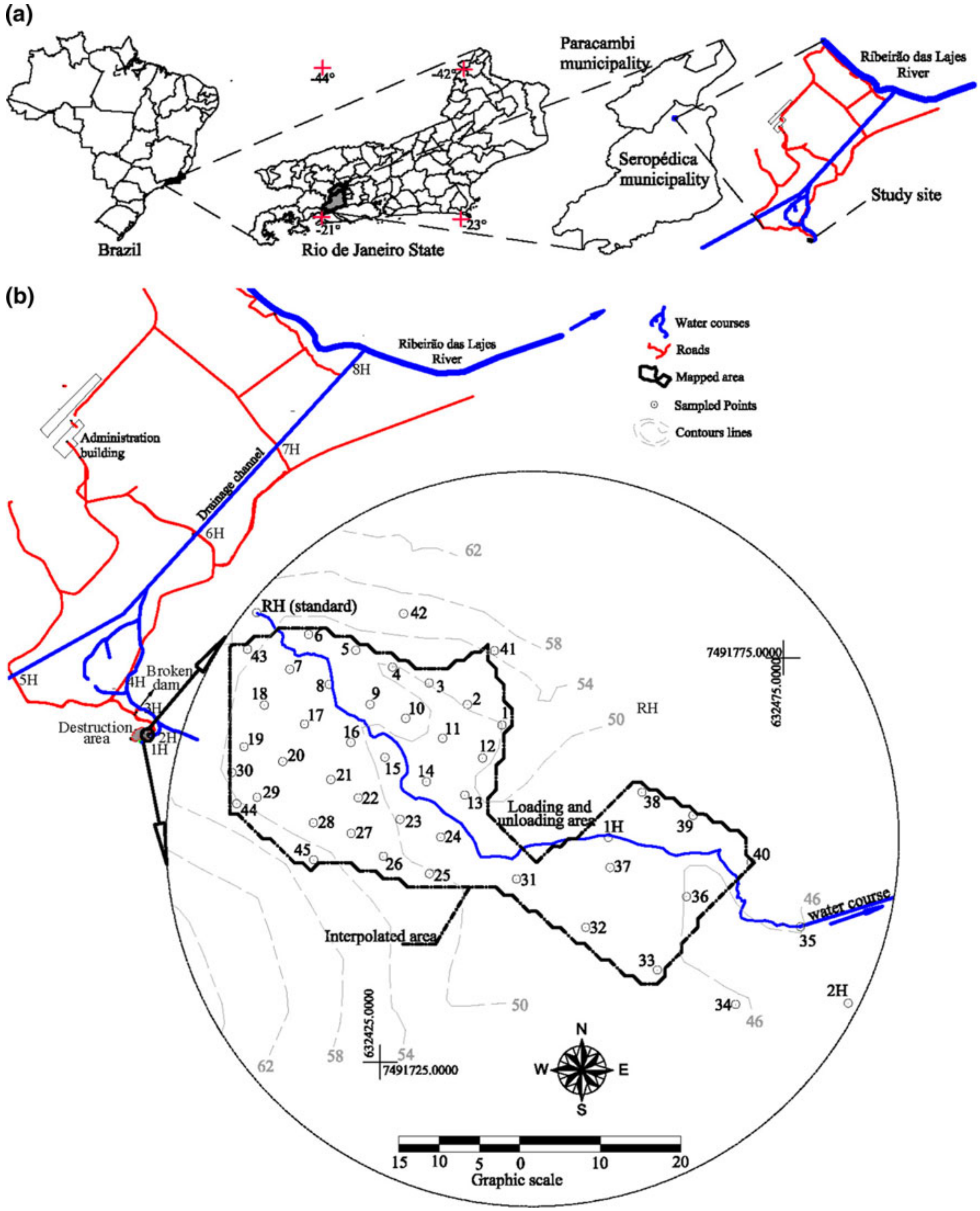

Fig. 1 Geographical location of the study area and ammunition destruction (**a**) and detailing of Ammunition destruction site with the sampling system following the 5 m × 5 m grid (**b**) (Color figure online)

The results demonstrated that the average lead value was 163 mg kg^{-1}, which was close to the investigation limit. The results showed a minimum value of 31 mg kg^{-1} (point 29 at the 40–60 cm depth) and a maximum value of 535 mg kg^{-1}, which was equivalent to approximately three times the investigation limit (point 12 at the 40–60 cm depth). When comparing the lead concentrations of the 30 points with the reference values according to CONAMA (2009), 37 % of the samples were greater than the investigation limit, 49 % were greater than the prevention limit, and only 14 % were below the prevention limit.

Regarding lead distribution at the different soil depths, higher concentrations were found in the surface layer depth, which included the destruction area, upstream and downstream sampling points. This trend corroborated previous studies by demonstrating that lead contamination was generally located in the uppermost soil layers (Cao et al. 2003; Li 2006). The low surface mobility and accumulation of lead have been reported in several studies (Al-Khashman and Shawabkeh 2009; Huang et al. 2011; Luo and YuS 2011). However, high lead concentrations were also found at deeper soil depths in the destruction area due to frequent detonations. When considering the sampling points with lead levels greater than the investigation limit, the following distributions of lead per soil depth were found: 34.5 % at 0–20 cm, 18.2 % at 20–40 cm, 16.4 % at 40–60 cm, 18.2 % at 60–80 cm, and 12.7 % at 80–100 cm.

In evaluating the surrounding areas of the destruction site, there was generally decreased lead contamination in the upstream and downstream points at the five soil depth layers (Fig. 1b). The following points stood out in the upstream area, especially at the surface layer: 44 (above the investigation limit), 41, and 43 (above the prevention limit). These points had even relatively higher values because they were situated on the edge of the destruction area (Fig. 1b). The contamination levels were higher downstream than upstream, which may have been due to the transport of lead-contaminated sediment runoff from the destruction area. Among the downstream points, 40, 37, 31, and 35 stood out for exhibiting levels greater than the investigation limit and were located closer to the natural drainage that crossed the entire study area (Fig. 1b). These results suggested that lead was carried by runoff (water drainage channel). Reduced lead levels in areas surrounding the location of highest activity have also been reported by other authors, including Silva et al. (2004), McGrath et al. (2004) and Amaral Sobrinho et al. (2009).

Although the destruction area and some marginal points exhibited high lead concentrations, contaminated surface water was found, especially at points 1H and 2H (Table 1 and Fig. 1b), which had higher concentrations. These values were higher than the standard value for drinking water (0.01 mg L^{-1}), and only point 1H exceeded the standard value for effluent discharge into water bodies (0.5 mg L^{-1}) (CONAMA 2005). Lead concentrations at the other points monitored throughout the area (3H through 8H) (Fig. 1b) were close to those at the reference point (RH). These results were consistent with those found for soil that had lead concentrations higher than the investigation value (CONAMA 2009) and that were under direct influence of ammunition destruction, thus characterizing the need for remediating the ammunition destruction site.

Table 1 Lead concentration (mg L^{-1}) in surface waters from nine sampling points

Standard (RH)	0.02	3H	0.001	6H	nd
1H	0.91	4H	nd	7H	nd
2H	0.05	5H	0.001	8H	0.001

nd not detected

Values represent the mean of three analytical replications

Considering lead contamination within the destruction area and at the surface layer depths, semivariograms for the 0–100 cm depth layers were calculated to assess spatial dependence. The lead dispersion values were quite high at all depths, which may be due to high variation coefficient values, especially at subsurface layer depths.

In general, lead exhibited a frequency distribution different than normal with values greater than 0.5 asymmetry in the module. For detecting structured semivariance, it was necessary to logarithmically transform to base 10 (Fig. 2). There was spatial dependence at all depths with predominance of the Gaussian model (20–40, 40–60, 60–80 and 80–100 cm) and the spherical model at the surface (0–20 cm). Thus, the spatial variability in the heavy metal concentrations within the area was not simply random, and the metals had entirely or partially structured semivariance. Similar results of lead spatial dependence were found by Silva et al. (2004) and by McGrath et al. (2004). The authors evaluated lead spatial distribution only on the surface (15 and 10 cm, respectively) and used fitted spherical semivariogram models.

Although spatial dependence demonstrated that the geostatistical interpolation was most appropriate, there were differences in the performance of the interpolators at increased depths. In general, the parameters for fitting models to experimental semivariograms, including nugget effect (C_0), range (a), sill ($C_0 + C_1$), spatial dependence index ($(C_0)/(C_0 + C_1)$), and r^2, are used for evaluating interpolation performance.

The best fits were found at depths of 0–20, 60–80, and 80–100 cm where there were smaller nugget effect (C_0) values and higher r^2 values. The short range (autocorrelation distance) at the 0–20 cm depth was also noteworthy, which implied that regions with relatively small radii were found throughout the site in which the lead levels were most similar. Capturing spatial dependence with only a range of 9.8 m demonstrated that the sampling grid used was adequate for modeling the data. The short distance also suggested that lead exhibited a spatial variability pattern closer to random at this depth and that the weights from each point used in the interpolation were more similar (Gringarten and Deutsch 2001). Finally, the low r^2 values at the soil depths of 20–40 and 40–60 cm did not necessarily imply that interpolation was lower at these layers because r^2 refers to model fit for all semivariance points and the model fitted to semivariance points within the range limit is what matters for geostatistical interpolation. Comparing these results with a study by Vieira (2000), it is possible to state that the semivariogram analyses for the evaluated chemical

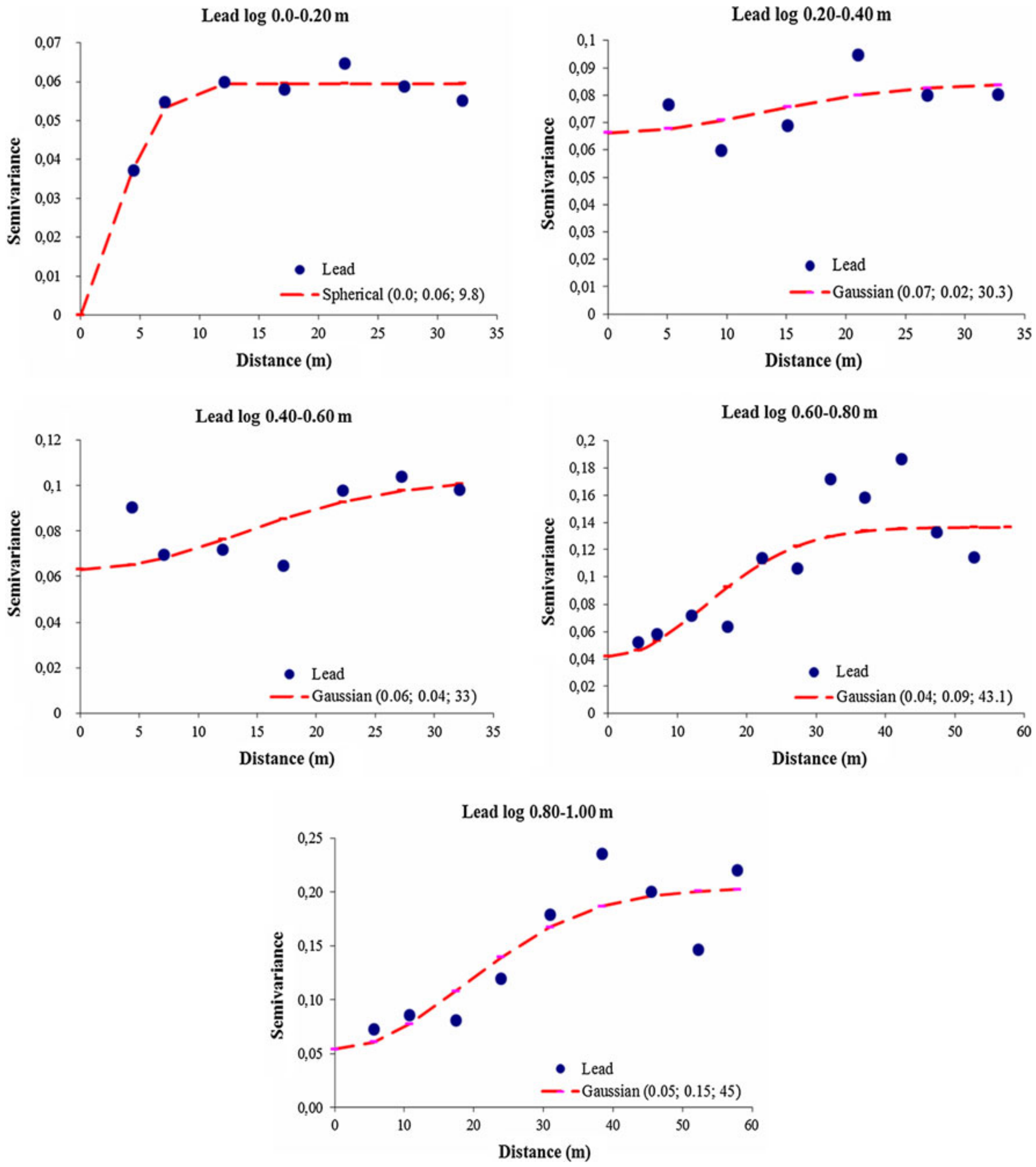

Fig. 2 Lead content semivariograms at different depths (Color figure online)

attributes did not indicate any preferred direction, i.e., the data were not anisotropic. Therefore, the spatial variability of the data occurred the same way in all directions.

The maps of lead spatial variability generated by ordinary kriging and planimetry are shown in Fig. 3, which shows the lead values as colors classified according to CONAMA as follows: clean area (*green*), prevention area (*blue*), and contaminated area (*red*). In addition to the maps helping in visualizing the substantially reduced contaminated area with increasing depth, the maps provided knowledge of what the geostatistics technique provided, thus allowing delimitation and precise calculation of areas needing remediation (lead content greater than 180 mg kg^{-1}). According to the planimetry data (Fig. 3), the areas that require intervention significantly decreased with increasing depths in the following order: 582.7 m^2 in the 0–20 cm layer; 194.6 m^2 in the 20–40 cm layer; 101.6 m^2 in the 40–60 cm layer; and 45.3 m^2 in the 60–80 cm layer.

The destruction area and surrounding areas, including areas both upstream and downstream, were contaminated

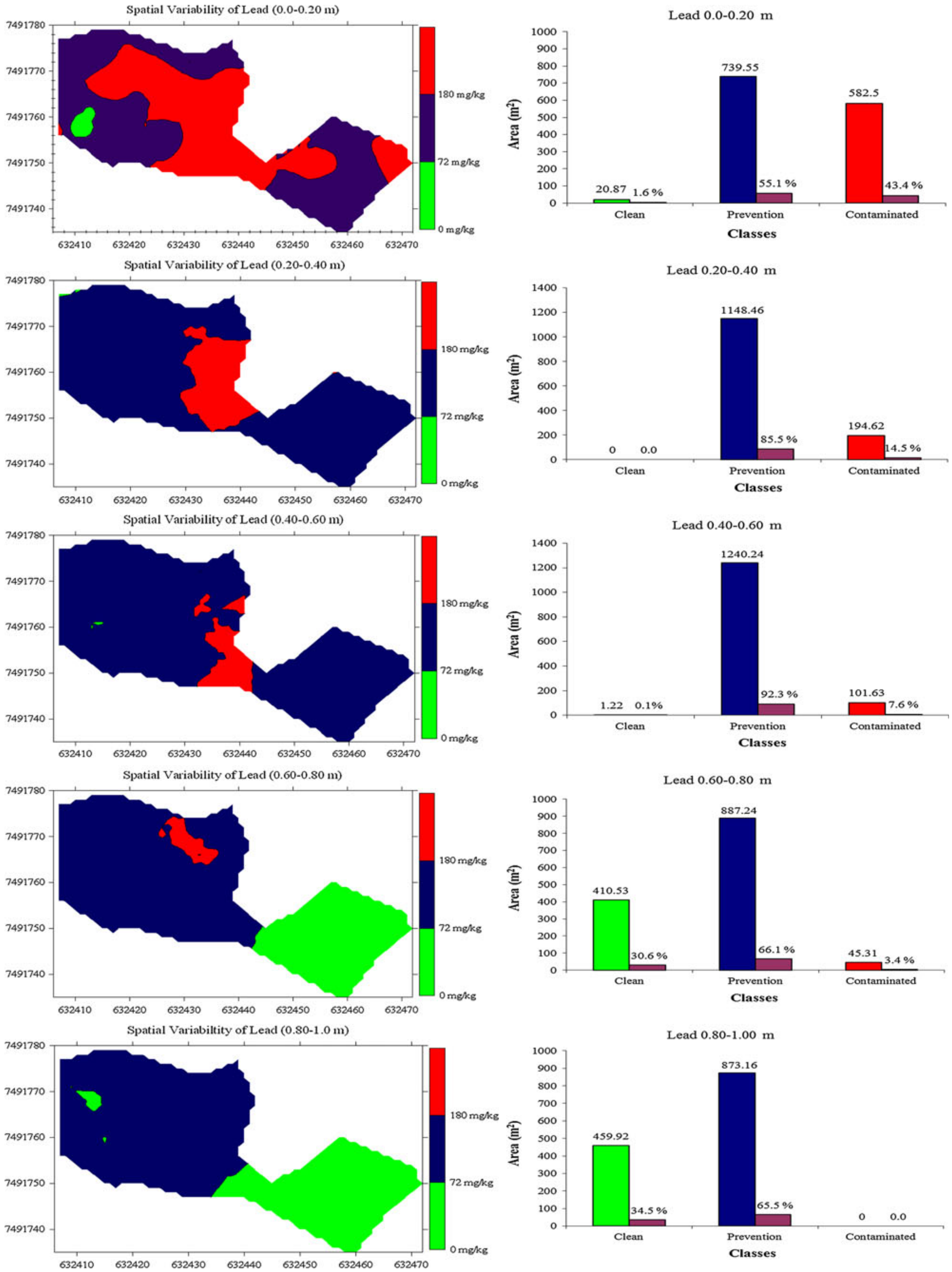

Fig. 3 Lead content Maps of spatial variability and planimetry at different depths (Color figure online)

with lead. Moreover, the lead content decreased with increasing depth, especially starting at the depth of 80 cm. The lead content in the surface water near the destruction area was greater than the quality parameters predetermined by CONAMA. However, the levels of lead substantially decreased throughout the drainage channel until the mouth of the channel where it was no longer detected. In this study, there was semivariance-structured spatial dependence, and the Gaussian and spherical models were the best fit. Furthermore, the spatial distribution of lead contamination was especially pronounced in the first 20 cm depth compared to the other depths.

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