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Dimensionality of heavy metal distribution in waste disposal sites using nonlinear dynamics

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Abstract

Mapping of heavy metal contamination in mining and waste disposal sites usually relies on geostatistical approaches and linear stochastic dynamics. The present paper aims to identify, using the Grassberger–Procaccia correlation dimension (CD) algorithm, the existence of a nonlinear deterministic and chaotic dynamic behaviour in the spatial pattern of arsenic, manganese and zinc concentration in a Russian coal waste disposal site.

The analysis carried out yielded embedding dimension values ranging between 7 and 8 suggesting thus from a chaotic dynamic perspective that arsenic, manganese and zinc concentration in space is a medium dimensional problem for the regionalized scale considered in this study.

This alternative nonlinear dynamics approach may complement conventional geostatistical studies and may be also used for the estimation of risk and the subsequent screening and selection of a feasible remediation scheme in wider mining and waste disposal sites.

Finally, the synergistic effect of this study may be further elaborated if additional factors including among others presence of hot spots, density and depth of sampling, mineralogy of wastes and sensitivity of analytical techniques are taken into account.

Keywords: Heavy metal distribution; Nonlinear dynamics; Geostatistics; Correlation dimension algorithms

1. Introduction

Activities associated with coal and mixed sulphide ore mining and beneficiation result in the production of huge volumes of reactive solid wastes and the subsequent generation of acidic leachates containing heavy metals and metalloids causing widespread contamination of soil, surface- and groundwater [1,2].

The assessment of the degree of soil and water contamination in wider mining and waste disposal sites is in general a quite complex procedure. The impacts depend among others on waste and leachate quality, land use, soil type, climatic conditions, population characteristics, precipitation rate, flow rate of the aquatic streams, depth of the aquifer and contaminant contact or ingestion rate; for example different impacts are anticipated in agricultural soils, soils present in residential or industrial areas, streams with a seasonal flow, shallow depth wells and confined or non-confined aquifers.

An important issue that has to be taken into consideration during risk and health assessment exercises is that only in a few countries exist thresholds for soil quality. For example Canadian guidelines classify contaminated soils according to their land use whereas Dutch guidelines provide target and intervention values. Another issue that has to be underlined is the lack of commonly used standard tests to classify wastes and leachates under specific environmental conditions [3,4].

Risk assessment involves calculation of ecological or health risk in mining, waste disposal, industrial, agricultural or residential areas as well as in ecosystems. The conventional methodology used is based on the principle "source—pathway—target" and accounts for spatial and temporal variability of contaminant patterns. A probabilistic assessment incorporates variability of parameters and uncertainty in measurement [5,6].

Geostatistics is used to predict the extent of soil and groundwater contamination as well as to calculate the risk in active or

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abandoned mining, waste disposal and urban sites, by preserving the spatial distribution and uncertainty of the estimates. It facilitates quantification of the spatial features of soil parameters and enables spatial interpolation [7–12].

Most geostatistical studies consider the concentration of a hazardous element in soils and other affected media as a regionalized variable in space and include computation and modeling of the variogram, prediction of the concentration in non-sampled areas by kriging and finally statistical analysis of errors [13–15]. Conventional geostatistical techniques manage to deal with the pattern completion problem but may not be able to solve the pattern recognition problem [16–19]. This is mainly due to the limited number of available samples, the lack of a properly designed sampling campaign, the extent of the study site, the presence of hot spots and the limited homogeneity seen due to the treatment of ores with varying quality using different techniques over long periods. When Geographical Information Systems are used the estimation of hazard and spatial uncertainty may be improved [20,21]. Care should be taken though when geostatistics is used to assess the risk in cases where hot spots or different types of wastes are present, especially in abandoned mining and waste disposal sites.

The calculation of soil risk takes into account generic standards (target and intervention values) that are used to assess soil quality and classify soils according to the extent of contamination. The target values are protective levels and indicate the desired soil quality while the intervention values are indicative of serious contamination [22]. The assessment of risk for the population is a much more complex procedure and requires the knowledge of exposure rates over various periods as well as the establishment of human toxicological and eco-toxicological intervention values. A generic methodology that combines quantitative probabilistic human health risk assessment and spatial geostatistical methods has been recently proposed [23]. This methodology enables the calculation of human health risk from exposure to contaminated land in a manner that preserves its spatial distribution and provides a measure of uncertainty in the assessment. Uncertainties in mapping the probability of soil contamination when various heavy metals are present should be taken into account; in addition a co-simulation technique involving direct sequential simulation of a multivariable set of variables may be used to establish a reliable “hazard index” for each part of the study area [24].

The geostatistical approach that assesses the concentration of a specific heavy metal in space as a regionalized random or stochastic variable may often result in an inaccurate prediction of its spatial variability in local and regional scale, due to the complexity of factors affecting the origin and fate of this specific contaminant in various media. A number of recent studies [25–28] examine the application of nonlinear deterministic dynamics that improves the accuracy of geostatistics by taking into account the synergistic action of factors such as disposal of different types of wastes in the same area, varying soil horizons, groundwater flow and transport phenomena.

Inorganic elements present in soils such as zinc, copper, manganese, nickel and molybdenum are micronutrients that are important constituents of enzymes and thus critical for the proper development of plant species. If the concentration of a specific element in soil exceeds a certain threshold then it becomes toxic to plants and inhibits their growth; in addition, if this element is taken up by the plants through the root system it may enter the food chain and become toxic to humans and animals [29].

The objectives of the present study are (a) to enable a distinction between a possible nonlinear or chaotic and a random behaviour, using the spatial pattern of three pollutants, namely arsenic, manganese and zinc in a wider coal waste disposal Russian site, (b) to assess the number of independent parameters affecting the underlying dynamic system that governs the mobilization of these contaminants and (c) to define the additional factors that should be taken into account to enhance the accuracy of the spatial estimation of heavy metals distribution. This study aims to complement, rather than replace, conventional geostatistical approaches and to consider the synergistic effect that minimizes potential limitations seen in other studies [30,31].

2. Methodology

2.1. Related notions from the theory of nonlinear dynamics

Several methodologies have been developed for the identification of chaotic behaviour in a data series as for example the Hausdorff, the box-counting and the information dimension. The correlation dimension (CD) method which is used in this study is considered as straightforward and is often in agreement with other methods that are used to calculate dimensions [32]. The CD method uses the correlation integral to distinguish between chaotic and stochastic behaviour (more specifically, between low- and high-dimensional systems). The concept of the correlation integral is based on the fact that even if a process governed by deterministic dynamics looks irregular (i.e. ‘random’), it has a limited number of degrees of freedom which are equal to the smallest number of first-order differential equations capturing the most important features of the dynamics. Earlier studies have examined the application of CD in hydrology, wastewaters flow and climatic changes [27,28,33,34].

Even though the most common CD applications involve processing of data series in the continuum of time, the algorithm has been successfully applied to data series in space where unequal delay distances are seen [35]. The main concern when the Grassberger–Procaccia algorithm is applied in space is the existence of up to three independent variables, instead of one, affecting thus the variability of the pollutant. If only the distance, instead of two spatial coordinates, is used as the independent variable, some isotropy is implied in the spatial pattern and this may bias results; this is not the case though in the present study [30].

With the above limitation in mind, the square sampling grid is converted to a data series first in the Y direction as seen in Fig. 1 and then accordingly in the X direction. The algorithm uses the phase-space reconstruction of this spatial series. For a scalar spatial series X_i, where $i = 1, 2, 3, \ldots, N$, (X_i is the arsenic concentration at sample point i), the phase-space can be

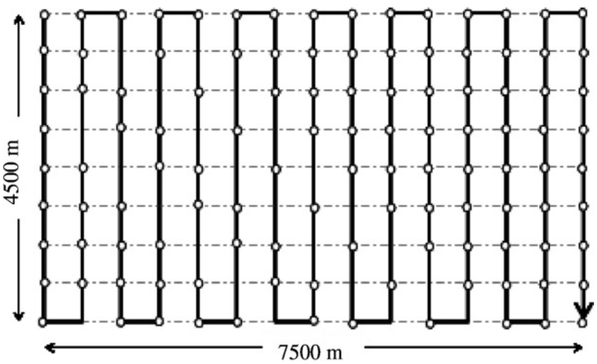

Fig. 1. Conversion of data grid to a data series by Y axis direction.

constructed using the method of delays (distances) presented as

$$Y_j = (X_j, X_{j+\tau}, X_{j+2\tau}, \ldots, X_{j+(m-1)\tau/\Delta s}), \tag{1}$$

where $j = 1, 2, \ldots, N-(m-1)\tau/\Delta s$; m is the dimension of the vector Y_j, also called embedding dimension; and τ is the delay distance as suitable multiplicate of the intra-sample distance Δs. For an m-dimensional phase-space, the correlation integral $C(r)$ is expressed as [36],

$$C(r) = \lim_{N\to\infty} \frac{1}{N^2} \times [\text{number of pairs } i, j \text{ whose distance} |Y_i - Y_j| <$$

This correlation function is written more formally if the Heaviside step function is used:

$$C(r) = \lim_{N\to\infty} \frac{1}{N^2} \sum_{i,j=1}^{N} H(r - |Y_i - Y_j|) \tag{2}$$

where $1 \leq i < j \leq N$; H is the Heaviside function with $H(u) = 1$ for $u > 0$ and $H(u) = 0$ for $u \leq 0$, where $u = r - |Y_i - Y_j|$, r is the radius of sphere centred on Y_i or Y_j and N is the number of sample points in the spatial series.

If the spatial series is characterized by an attractor, then for a limited range of r it is seen that:

$$C(r) \propto r^{\nu} \tag{3}$$

where ν is the correlation exponent or the slope of $\ln C(r)$ versus $\ln r$ plot, expressed as

$$\nu = \lim_{(r\to 0, N\to\infty)} \frac{\ln\ C(r)}{\ln\ r} \tag{4}$$

The slope is generally estimated by a least-squares fit of a straight line over a certain range r, called the scaling region.

The scaling of the correlation integral $C(r)$ (i.e. the dimensionality of the attractor) is defined by its slope in the $\ln C(r)$ versus $\ln r$ diagram [37]. When the embedding dimension m increases, the slopes of the related curves tend towards a limiting or saturation value, unless the underlying dynamics is a random process. This saturation value defines the dimension of the attractor and a lower bound for the number of independent variables to simulate dynamics. Thus, in case when the value of the correlation exponent is small, the system is mainly dominated by a low-dimensional dynamics (spatial) governed by the properties of an attractor. The saturation value of the correlation exponent is defined as the CD of the attractor of the spatial series. In contrast, for systems dominated by stochastic processes, the correlation exponent is supposed to increase without any bound.

However, while this type of interpretation is generally considered to distinguish between chaotic and random behaviour, there may also be certain exceptions, since the existence of a finite correlation dimension is not a sufficient condition for the existence of an attractor. As it turns out though, this may have no relevance to the practical estimation of dimensions from time series. The concept of fractal dimension can be applied to time series in two distinct ways, either to indicate the number of degrees of freedom in the underlying dynamic system, or to quantify the self-similarity of the trajectory in phase-space.

2.2. Description of the site—data configuration

The area under study belongs to the wider coal mining and waste disposal region of Tula, 200 km south of Moscow, Russia. Fig. 2 shows the main mineralogical phases present in the wastes. The concentration of the main trace elements varies between (in mg/kg): As 10–200, Cr 50–300, Mn 100–1600, Pb 10–90, Cu 10–500, Zn 70–3000, Ni 50–300, Co 20–50, Sr 70–200 and Se 1–4. Additional information regarding the site, the characteristics of the wastes, the potential for generation of acidic leachates and the environmental impacts can be seen in a previous publication [30].

135 surface samples were collected (in duplicate) from a depth of 20 cm using a square 500 m × 500 m grid. The total area sampled was 34 km^2 (4.5 km × 7.5 km), corresponding to a sampling density of 4 samples/km^2 and covering not only the waste disposal site but also the surrounding cultivated areas. The samples were oven-dried, sieved, ground, dissolved in aqua regia and analyzed by flame atomic absorption spectrophotometry (PerkinElmer 2100) for 23 inorganic elements, using Sigma–Aldrich standards. In a limited number of samples, where the measurement error exceeded 5%, digestion and measurements were repeated. The statistical analysis, including minimum, maximum, mean, median, standard deviation, as well as the 5, 95 and 99 percentiles, of As, Mn and Zn concentration

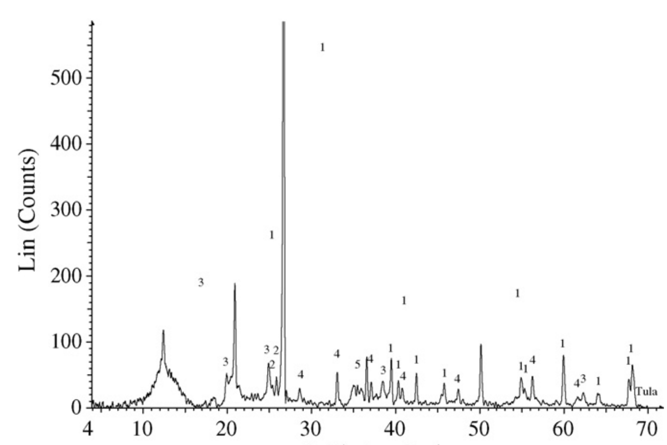

Fig. 2. XRD pattern of Tula wastes: (1) quartz, (2) aragonite, (3) kaolin, (4) pyrite, and (5) magnetite.

Table 1
Statistical analysis of As, Mn and Zn concentration (mg/kg)

Element	Mean	Standard deviation	Minimum	5%	Median	95%	99%	Maximum
As	17.4	3.9	9.3	13	17	25	32	36
Mn	840.5	142.9	115	494	839	1182	1380	1540
Zn	164.5	122.2	1	23.9	129	406	510	749

Table 2
Russian, Canadian and Netherlands thresholds for heavy metal concentration in soils (mg/kg)

	Russian			Canadian			Netherlands	
	Sandy soil	Sour soil pH <5.5	Neutral soil pH >5.5	Agricultural land	Residential area	Industrial area	Target values	Intervention values
As	2	5	10	12	12	12	29	55
Zn	55	110	220	200	200	360	140	720

(in mg/kg) are seen in Table 1. The Russian Tentative Allowable Concentration limits (TAC) for agricultural soils as well as the Canadian [38] and Netherlands [22,39] thresholds for heavy metals concentration in soils are seen in Table 2. No thresholds for manganese exist either in the EU or Russian legislation; the reason may be that manganese occurs naturally in relatively high concentrations in soils.

Analysis of the samples shows that 132 As values (97.8%) and 33 Zn (24.4%) exceed the Russian TAC for neutral soils [30]. These percentages are in fact higher since a number of soil samples are quite sour. Therefore As and Zn as well as Mn, due to its toxicity and high mobility, will be further studied in detailed. It should be underlined that 129 As values (95.56%) and 38 Zn (28.15%) exceed the Canadian guidelines for agricultural soils whereas only one Zn (0.74%) and no As values (0%) exceed the Netherlands intervention values. To further underline the complexity in this issue, it is mentioned that the UK guidelines suggest as maximum tolerable limit for As in soil 20 mg/kg.

Of the three elements studied, the most important for coal mining and waste disposal sites is manganese, which due to its high mobility migrates easily and contaminates surface streams and groundwater. Its favored oxidation stages are II, III and IV, while its oxidation and precipitation is more efficient at high pH and Eh values [40,41]. Manganese is not considered as ecotoxic as other common contaminants such as Fe, Al and Zn but it is one of the most difficult to remove pollutants from acidic leachates generated in coal waste disposal sites. Under mild oxidizing conditions Mn is in the +4 valence state and forms an insoluble precipitate, MnO_2, while under reducing conditions is converted to the +2 valence state and is present as soluble Mn^{2+} cation. The concentration of dissolved Mn in solutions (leachates) generated in coal waste disposal sites may be determined by the precipitation of amorphous pyrocroite, $Mn(OH)_2$. Sorption and ion-exchange are processes that affect dissolved Mn concentration and assess the severity of groundwater contamination when manganese containing leachates infiltrate soils and other formations overlying the aquifer [42].

3. Results and discussion

3.1. Evidence of chaotic behaviour

A first evidence of chaotic behaviour is seen from the covariance functions of arsenic, manganese and zinc concentrations [30], which exhibit cycling fluctuations after reaching their sill value [35]. Phase portrait is a valuable tool that can be used to assess data behaviour, either random or chaotic [36]. Such phase portraits of the different contaminant concentrations were drawn in two and three dimensions, as described in the previous section. An appropriate delay distance τ equal to 1500 m was employed, using the length that the covariance function takes the first zero value [34]. These phase portraits, seen in Figs. 3 and 4 for As and Mn respectively, indicate a chaotic rather than a pure noise behaviour.

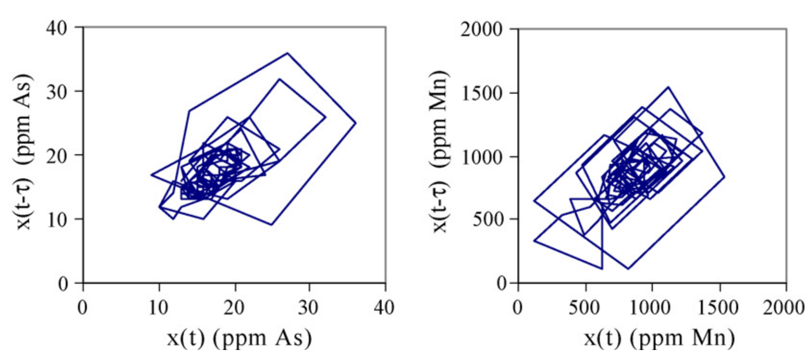

Fig. 3. Phase portraits of As and Mn concentrations.

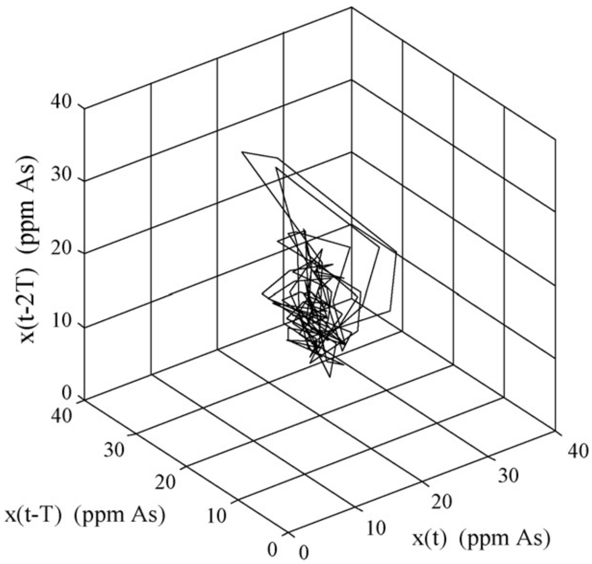

Fig. 4. 3D phase portrait of As concentrations.

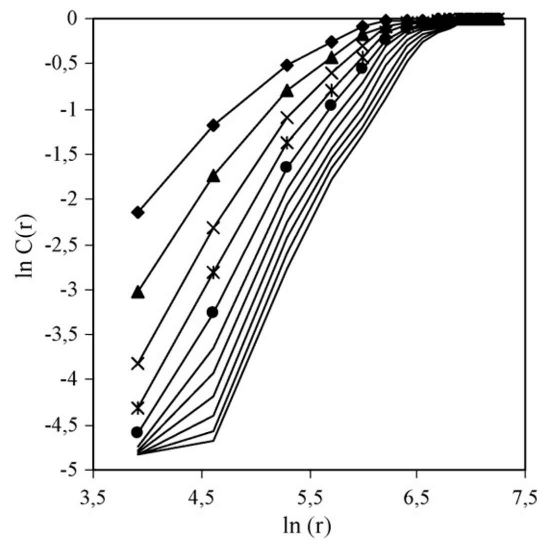

Fig. 6. Relationship between ln $C(r)$ and distance ln(r) for Zn.

A similar behaviour is seen for Zn and for most other contaminants present in wastes (data not shown).

3.2. Correlation dimension analysis

In order to elaborate the relationship between correlation exponent and embedding dimension, all contaminant concentrations were first converted to data series in each Y and X directions respectively, as seen in Fig. 5 for As. This as well as the following similar figures created following the steps described in detail in the previous section. The saturation of slope ln $C(r)$/ln(r), seen in Figs. 6–8, provides evidence of possible nonlinear deterministic and chaotic dynamic behaviour [25,35]. This calculated saturation correlation exponent value (also known as CD) is almost identical in each X or Y direction, as seen in Fig. 5 for the concentration of As; therefore in the respective figures no conversion results are presented for Zn and Mn in the second direction.

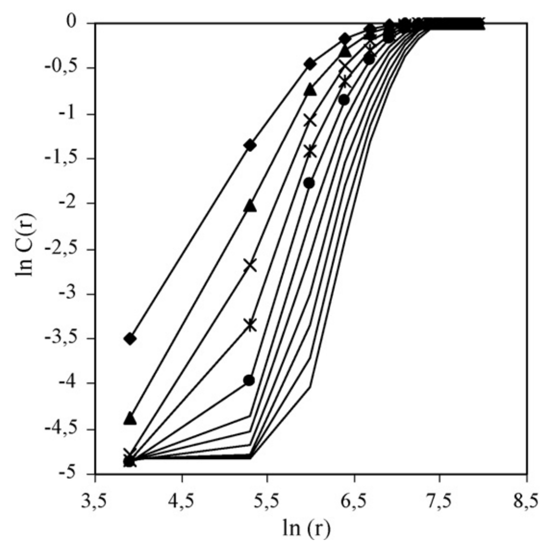

Fig. 7. Relationship between ln $C(r)$ and distance ln(r) for Mn.

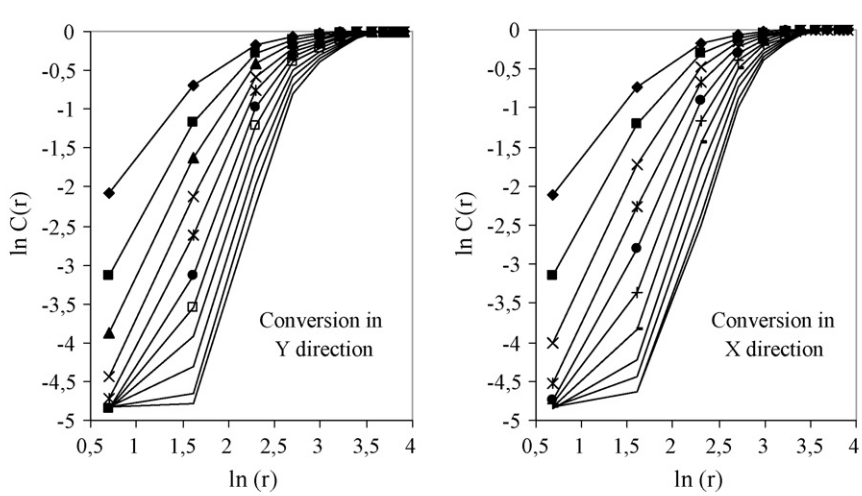

Fig. 5. Relationship between ln $C(r)$ vs. distance ln(r) in Y and X conversions for As.

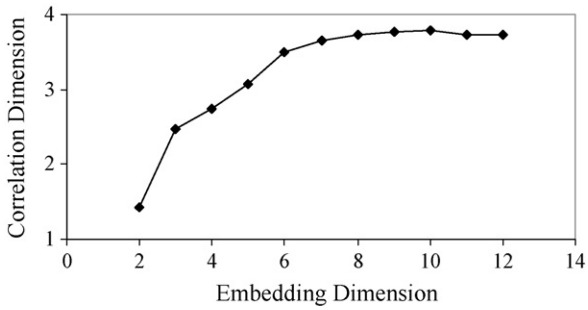

Fig. 8. Relationship between correlation dimension and embedding dimension for As.

The As CD value lies between 3 and 4 while the embedding dimension at which this saturation occurs is almost 8 (Fig. 5). The CD for Zn and Mn concentrations ranges between 2–3 and 3–4 respectively, while the embedding dimension for both metals is almost 7 (Figs. 6 and 7). This again indicates that a medium model structure is required to adequately capture the spatial variability of Zn and Mn.

3.3. Spatial variability

The results of the present study indicate that a medium model structure, including 7–8 model parameters, is required to adequately capture spatial variability of arsenic, manganese and zinc concentration at the regionalized scale used in this waste disposal site (500 m × 500 m). These results are similar to those presented in an earlier publication, where geostatistics under the maximum entropy principle was considered [30] and confirm the validity of the conversion model used.

The fact that the number of dimensions that assess the spatial distribution is almost equal for all elements, might suggest that the dominant processes involved so far in solubilisation and transport of pollutants in the waste disposal site under study are similar. This was somehow anticipated for all three elements, due to their presence in the organic part of the wastes; no traces of arsenopyrite or zinc/manganese minerals were detected either in the native ore or in the beneficiation wastes [43]. The effect though of physical (e.g. rain, wind) or chemical/biological factors (e.g. soil pH, presence of bacteria) that determine transfer and therefore spatial variability of contaminants cannot be easily assessed at this stage; the chaotic behaviour of these contaminants can be better defined if the contribution of additional factors mentioned below is well known.

The synergistic effect of this approach on current geostatistical techniques used for spatial characterization and risk assessment in mining and waste disposal sites may be further elaborated if the following issues are considered:

- density of sampling; the presence of hot spots over a large area may influence the spatial pattern of contaminants so that a chaotic behaviour is anticipated.
- Sampling depth; it may influence the chaotic behaviour of a contaminant concentration; it is well known that some contaminants may be solubilised from surface and precipitate again in deeper soil horizons. The cost effectiveness of deeper sampling should be also further explored.
- Soil properties (e.g. moisture content, grain size, degree of compaction, content of clay minerals); they affect the concentration and enhance/inhibit migration of contaminants.
- Mineralogy of the wastes; it may be used for the prediction of the extent of erosion as well as of the degree of solubilisation and potential migration of contaminants; the degree of solubilisation for contaminants present in wastes is also affected by the beneficiation method used—the use of chemicals for example makes the surface of the grains more reactive and therefore susceptible to attack by various leaching agents.
- Form of sulphur (sulphide, sulphate or organic); in acid generating wastes it may be used to predict the net neutralization potential and the degree of secondary solubilisation of contaminants; it is well known that only sulphide sulphur participates in acid generation reactions.
- Sensitivity of analytical techniques used to determine the concentration of contaminants in various media, especially when the thresholds are low (ppb scale).

All the above-mentioned factors may well influence the chaotic behaviour of a contaminant concentration and subsequently the selection and cost effectiveness of a feasible rehabilitation scheme.

4. Conclusions

The present paper aims to identify, using the Grassberger–Procaccia correlation dimension algorithm, the existence of a nonlinear deterministic and chaotic dynamic behaviour in the spatial pattern of arsenic, manganese and zinc contamination in a Russian coal waste disposal site. This is a problem of great practical interest in similar sites, since in most cases sampling is not dense or according to a properly designed sampling campaign.

The analysis carried out yielded embedding dimension values ranging between 7 and 8 suggesting thus from a chaotic dynamic perspective that arsenic, manganese and zinc concentration in space is a medium dimensional problem for the regionalized scale considered in this study.

The fact that the number of dimensions that assess the spatial distribution is almost equal for all elements, might suggest that the dominant processes involved so far in solubilisation and transport of pollutants in the waste disposal site under study are similar. This situation may change in the future when chemical and or biological processes are initiated or accelerated. Evolution of such processes mainly depends on climatic conditions, permeability and degree of saturation of wastes. Low temperature for example hinders bacterial activity and slows down the degree of contaminant solubilisation.

Finally, it should be underlined that this study complements rather than replaces conventional geostatistical approaches and considers a synergistic effect that minimizes potential limitations encountered in other studies. This synergistic effect may be further elaborated if additional factors including among others presence of hot spots, depth and density of sampling, mineralogy of wastes and sensitivity of analytical techniques are taken into account. Assessment of the impact of these factors will enhance accuracy of contamination mapping, quantification of risk and ultimately selection of a cost effective and feasible rehabilitation scheme.

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