



Applicability and limitations of the radon-deficit technique for the preliminary assessment of sites contaminated with complex mixtures of organic chemicals: A blind field-test



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ABSTRACT

A blind field test with 136 independent measurements of radon (^{222}Rn) in soil air retrieved from a depth of 0.8 m in a decommissioned lindane (γ -hexachlorocyclohexane) production plant was undertaken to evaluate the performance of the ^{222}Rn -deficit technique as a screening methodology for the location and delineation of subsurface accumulations of complex mixtures of organic contaminants. Maps of ^{222}Rn iso-concentrations were drawn and interpreted before direct analytical information regarding concentrations of hexachlorocyclohexanes, chlorobenzenes and BTEX compounds in soil, groundwater and soil air were disclosed to the authors. The location and extension of pollution hot spots inferred from the ^{222}Rn campaigns agrees remarkably well with the analytical data obtained from the intrusive sampling campaigns and with the location of contaminant source zones (chemical reactor and waste-storage area) and geological sinks of those contaminants (paleochannel). Two main limitations to the applicability of the ^{222}Rn -deficit technique were identified and assessed: The statistically significant variation of ^{222}Rn concentrations with diurnal changes of ground-level air temperature and the maximum depth of investigation in the absence of significant advective and co-advective transport of radon. If the influence of those two factors is accounted for and/or minimized (by averaging replicated measurements during the workday and in different days), the ^{222}Rn -deficit technique has the potential to be an efficient technique which delivers information in quasi-real time, with a much higher spatial density than that of intrusive techniques, at a much faster rate and at a significantly lower cost.

Main findings: The ^{222}Rn -deficit technique is an effective tool for real-time site characterization only limited by diffusion length of radon and diurnal temperature variations.

1. Introduction

Site characterization can be defined as the process of obtaining information about a site from scientific data collected in the field (Tetra Tech Environmental Management, 1997). Site characterization is the foundation of all decisions about the environmental state of the site and the uncertainties introduced at this stage will be magnified during the site evaluation and remediation processes and may result in a very inefficient allocation of resources. The conventional approach to site characterization involves drilling a limited number of boreholes, retrieving and sampling soil cores at discrete intervals, installing monitoring wells in some or all of those boreholes and collecting samples of groundwater from them. The analytical data thus obtained is of very

high quality, but it represents only the environment immediately around the borehole. In the absence of prior information about the location and extension of the contamination process, it is possible to position the boreholes and monitoring wells at points where they will produce useless or misleading data, increasing the costs of remediation and monitoring programs (Cohen et al., 2016; García-González et al., 2008).

The case of complex mixtures of chemical compounds, especially if they give rise to dense non-aqueous phase liquids (DNAPLs), is particularly challenging. Migration patterns of these mixtures in the vadose and saturated zones are often quite complex, following fractures and preferential pathways, and forming ganglia and small isolated lenses which are very difficult to discover and delineate using standard

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investigation techniques (borings and monitoring wells) due to their small size and intricate spatial distribution (Fernández et al., 2013; Kram et al., 2001).

Unconventional characterization methods like the radon (^{222}Rn)-deficit technique are meant to supplement and optimize the conventional approach by providing dense spatial information in quasi-real time, and at a reasonable cost. ^{222}Rn is present in all soils and groundwater and it is easy to detect on-site, fulfilling all the requirements for its application as a natural tracer (Schubert, 2015). The omnipresence of ^{222}Rn is an important advantage over soil gas monitoring (e.g. Bishop et al., 1990) in sites where Volatile Organic Compounds (VOCs) are not detected due to the age or nature of the contamination process.

^{222}Rn migrates from the subsoil to the ground surface through diffusion and advection (Schubert, 2015). Under the influence of significant barometric gradients, advection would be predominant over diffusive transport (Yakovleva and Parovik, 2010) in materials with high air permeability (i.e. fractures) (Etiope and Martinelli, 2002; Richon et al., 2011; Scanlon et al., 2002). In the absence of fractures and preferential flow paths, the effect of barometric gradients is limited to the top of the soil profile (i.e. a depth of less than 1 m) (Antonopoulos-Domis et al., 2009; Thomas et al., 1992). ^{222}Rn advective transport is predominant over diffusion in tectonically active regions, associated with the migration of carrier gases (i.e. CO_2 , CH_4 , N_2) whereas diffusive transport of ^{222}Rn is the main transport mechanism at a local spatial scale (Etiope and Martinelli, 2002; Kristiansson and Malmqvist, 1987). In the course of advective ^{222}Rn migration, both soil and bedrock act as a source of this element (Cohen et al., 2016; Cothorn and Smith, 1987) making it difficult to distinguish whether ^{222}Rn comes from a deep or shallow subsurface source with a single measurement of soil air (Richon et al., 2011). In summary, the magnitude of the concentrations of ^{222}Rn in soil air and their variability will be the result of the joint effect of the relative contribution of advection and diffusion, of spatial variations of lithology and of the temporal and spatial variations of NAPL and pore-water saturation in the vadose zone.

A comprehensive review of the use of ^{222}Rn as a natural tracer to assess subsurface NAPL contamination is presented in Schubert (2015). In homogeneous and uncontaminated subsoils, ^{222}Rn concentration in soil air and groundwater decreases only by exhalation (diffusion and advection) into the atmosphere. Thus, in the absence of lithological variations, lateral and temporal ^{222}Rn anomalies can be used as indicators of processes that influence subsurface ^{222}Rn emanation. The presence of organic phases in the migration path of ^{222}Rn results in a reduction of its concentration in soil air given the preferential partition of ^{222}Rn in the organic phase (Höhener and Surbeck, 2004; Schubert, 2015; Schubert et al., 2007b, 2002; Weiss, 1980). Consequently, reductions of ^{222}Rn concentrations in soil air relative to the local natural background should be indicative of the presence of high saturations of NAPL in the subsoil, and the analysis of the spatial distribution of ^{222}Rn activity in soil air at the site could be used to identify NAPL hotspots and to monitor their abatement during remediation processes (Castelluccio et al., 2018; De Simone et al., 2017, 2015; García-González et al., 2008; Hunkeler et al., 1997; Schubert et al., 2007a, 2005, 2002, 2001; Semprini et al., 2000; Semprini and Istok, 2006).

Previous studies have demonstrated the usefulness of the ^{222}Rn -deficit technique as a screening tool in sites with homogeneous lithology affected by light NAPLs (Barbosa et al., 2014; Castelluccio et al., 2018; De Simone et al., 2017; Galhardi and Bonotto, 2012; García-González et al., 2008; Schubert et al., 2011; Yoon et al., 2013). Other authors have interpreted ^{222}Rn measurements in groundwater samples affected with dissolved chlorinated compounds (tri- and tetrachloroethene, TCE and PCE) (Chen et al., 2014; Davis et al., 2003, 2002; Starr, 2007; Yoon et al., 2013) and BTEX (Galhardi and Bonotto, 2012) as indications of DNAPL and LNAPL residual saturation respectively. To the authors' best knowledge, however, the temporal and

spatial variability of ^{222}Rn concentrations in soil air and the uncertainties arising from sampling and analytical methods have not been sufficiently evaluated to validate the ^{222}Rn -deficit technique as a screening tool in sites affected with complex mixtures of organic chemicals.

The study presented in this manuscript was designed as a blind test of the field performance of the ^{222}Rn -deficit technique: No information about the location and extent of the hot spots of contamination at the study site was disclosed to the authors until the sampling and analysis campaigns were completed and their results interpreted in terms of the spatial distribution of sub-surface contamination. The ultimate goals of the study were (1) to assess the applicability of the ^{222}Rn deficit technique in a site contaminated with a complex mixture of organic compounds and (2) to evaluate the uncertainties in ^{222}Rn signal interpretation due to temporal and analytical variability.

2. Methods and materials

2.1. Study area

The blind test was conducted at the abandoned premises of a chemical company which for almost twenty years manufactured lindane (γ -hexachlorocyclohexane or γ -HCH) for its use as insecticide in agriculture and for the treatment of parasites in livestock and humans. It is estimated that the plant generated approximately 6800 t/year of solid wastes and between 300 and 1500 t/year of liquid wastes while it was in operation. Within the boundaries of the plant, solid wastes were stored directly on the deteriorated paved surface of the premises until they were transported to two nearby landfills, and liquid raw materials and by-products infiltrated and accumulated below the ground surface giving rise to high concentrations of benzene, xylenes, phenol, chlorobenzenes and co-dissolved lindane and non-commercial HCH isomers.

From a litho-stratigraphic perspective, the plant sits atop a quaternary alluvial terrace, made up of gravel interspersed with variable contents of clay and silt, and underlain by Eocene marls. The uneven contact between the alluvial materials and the marl reflects the paleo-surface resulting from fluvio-glacial dynamics. The depth to the roof of the marl formation, which acts as an impermeable layer, varies from less than 2 m below ground surface (m.b.g.s.) in the eastern section to approximately 4 m.b.g.s. in the depression (paleochannel) to the centre-west of the study area (Fig. 1). The results of a Ground-Penetrating Radar campaign and the litho-stratigraphic columns from 9 boreholes and 13 trial pits revealed neither lateral changes of lithology or texture, nor significant heterogeneities or void spaces within the alluvial materials or in the marl formation. There is no permanent groundwater table at the site: Rainwater infiltrates and accumulates in the alluvial materials only during the rainy season.

2.2. Sampling and analytical methods

A network of permanent soil air sampling probes was installed before the first of three field campaigns took place (Fig. 1). Each probe consisted of a 50 mm external-diameter PVC tube inserted into the ground to a depth of 0.8 m. The bottom 0.5 m section of the tube was perforated to allow the entry of soil air into the probe. Above ground, the probe's external diameter was reduced to 20 mm and equipped with an air-tight exit valve which was opened only for purging and sampling. Before sampling, the probes were purged with a vacuum pump for 1 min. Samples were retrieved with a 150 mL syringe equipped with a PTFE particle and a desiccant (DrieriteTM) filters to prevent the entry of particles and of excess moisture into the ionization chamber. The syringe was subsequently connected to the detachable ionization chamber of a pulse ionization ^{222}Rn detector RM-2 (RADON v.o.s.®). Vacuum was applied to the ionization chambers prior to the introduction of the soil air sample. Once the syringe was connected, the tap of the ionization chamber was opened, and the air sample was drawn into the

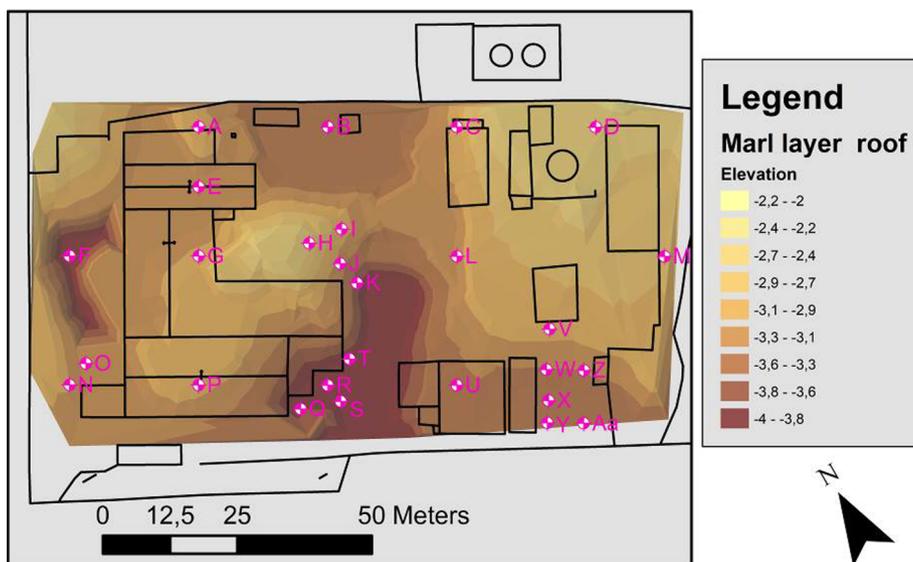


Fig. 1. Soil air sampling grid at the study site and depth to marl layer.

Table 1
Summary of ²²²Rn determinations (Bq/m³) at the study site.

Summary of data per campaign					
Campaign	No. Measurements	Sampled positions	Mean ²²² Rn (Bq/m ³)	sd	CV(%)
1	27	25	18,300	13,000	71%
2	89	22	20,600	11,400	56%
3	20	4	14,800	12,300	83%
Summary of field replicates					
Campaign	Sampling point	Mean ²²² Rn (Bq/m ³)	sd	CV(%)	No. Replicates
1	Aa	400	424	106%	2
	Y	13,900	3040	22%	2
2	A	40,500	2330	6%	3
	Aa	8680	4830	56%	4
	B	26,400	4670	18%	3
	C	28,800	2380	8%	3
	D	22,600	4950	22%	3
	E	18,800	4740	25%	3
	G	30,700	4660	15%	3
	H	36,500	3690	10%	3
	I	34,200	4800	14%	3
	J	40,900	1060	3%	2
	K	15,800	13,400	85%	5
	L	33,600	11,400	34%	4
	M	11,400	2320	20%	5
	N	32,500	8090	25%	3
3	P	15,500	9480	61%	3
	Q	12,200	7510	61%	6
	S	7400	7090	96%	5
	T	20,500	2790	14%	6
	U	14,500	1190	8%	3
	V	27,600	4710	17%	3
	W	13,900	5930	43%	6
	Y	20,800	4950	24%	5
	Z	7160	3760	52%	5
	C	33,800	3640	11%	5
	Q	5180	4030	78%	5
W	8500	7170	84%	5	
Y	11,700	3650	31%	5	

chamber by the negative pressure inside.

Measurements are based on the electric potential difference generated between the outside of the metallic ionization chamber (positively charged) and an electrode placed along the longitudinal axis (0 V). Alpha particles generated during the decay of ²²²Rn inside the chamber create a measurable electrical signal that is translated to radon activity

expressed in Bq/m³. The RADON v.o.s.[®] RM-2 detector was factory calibrated and the stability of its measurements was verified against a SARAD[®] RTM 2100 alpha-spectrometer. No measurement drift was detected and the absence of systematic errors was confirmed. However, a formal calibration with an absolute ²²²Rn standard was not performed and therefore all measurements in this study must be interpreted in

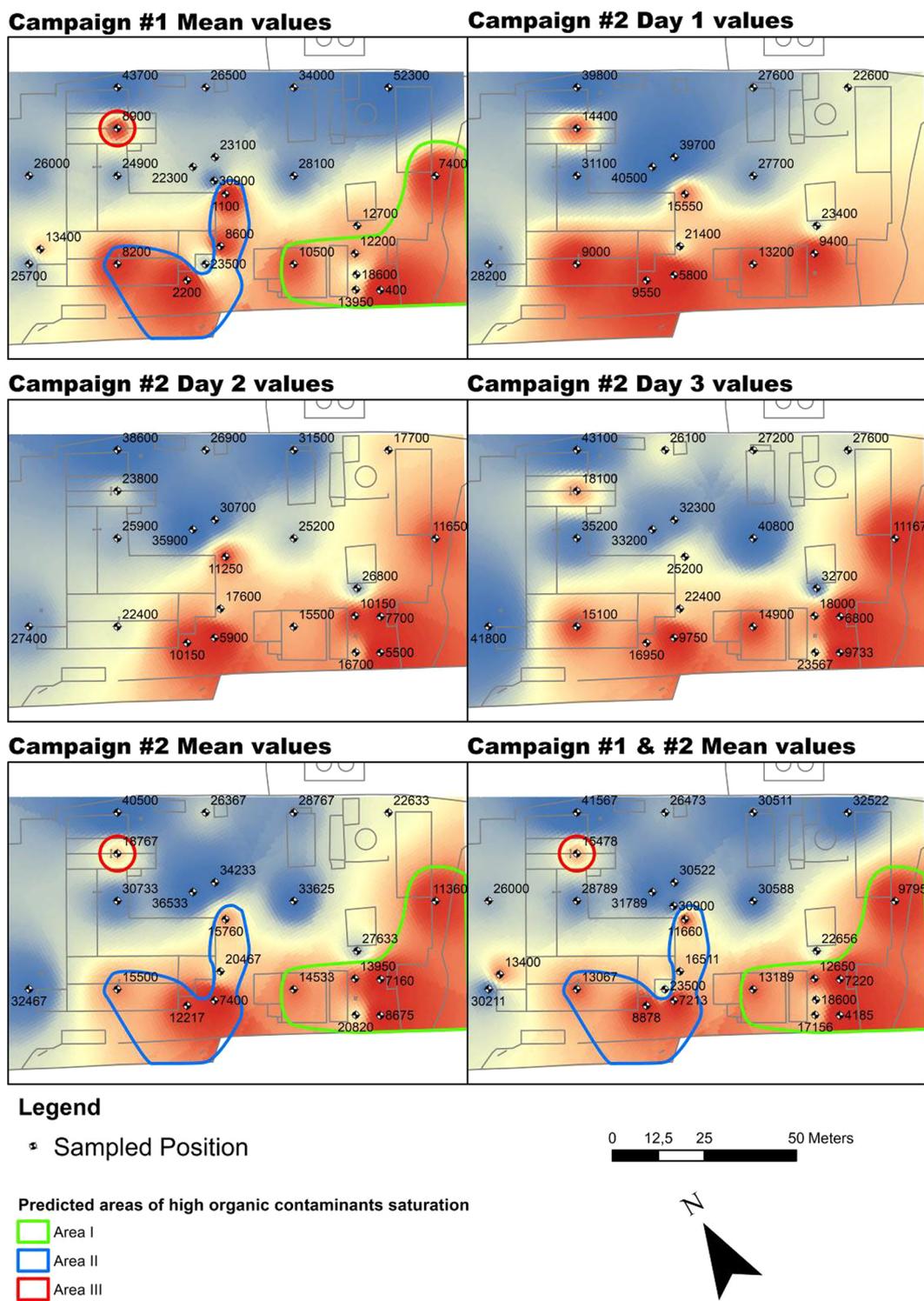


Fig. 2. ²²²Rn activity surface maps.

relative terms.

The spatial distribution of ²²²Rn measurements was compared with results of direct analyses of HCHs in subsoils (at 2 m.b.g.s. or deeper), dissolved organic compounds in groundwater and volatile organic compounds (VOCs) in soil air. The results of these analytical determinations were provided by the regional environmental authorities once the maps of ²²²Rn iso-concentrations had been produced and interpreted in terms of hot-spot detection and delineation.

3. Results

Three sampling and analytical campaigns were undertaken at the study site in April (Campaign #1), September (Campaign #2) 2017, and in October 2018 (Campaign #3) during which a total of 136 independent ²²²Rn measurements were obtained. The last campaign was entirely devoted to the assessment of diurnal variations of ²²²Rn activity at the site. In order to avoid the potentially confounding effect on ²²²Rn emanation of a varying soil pore-water saturation, and to make all measurements comparable, at least one week was allowed to pass

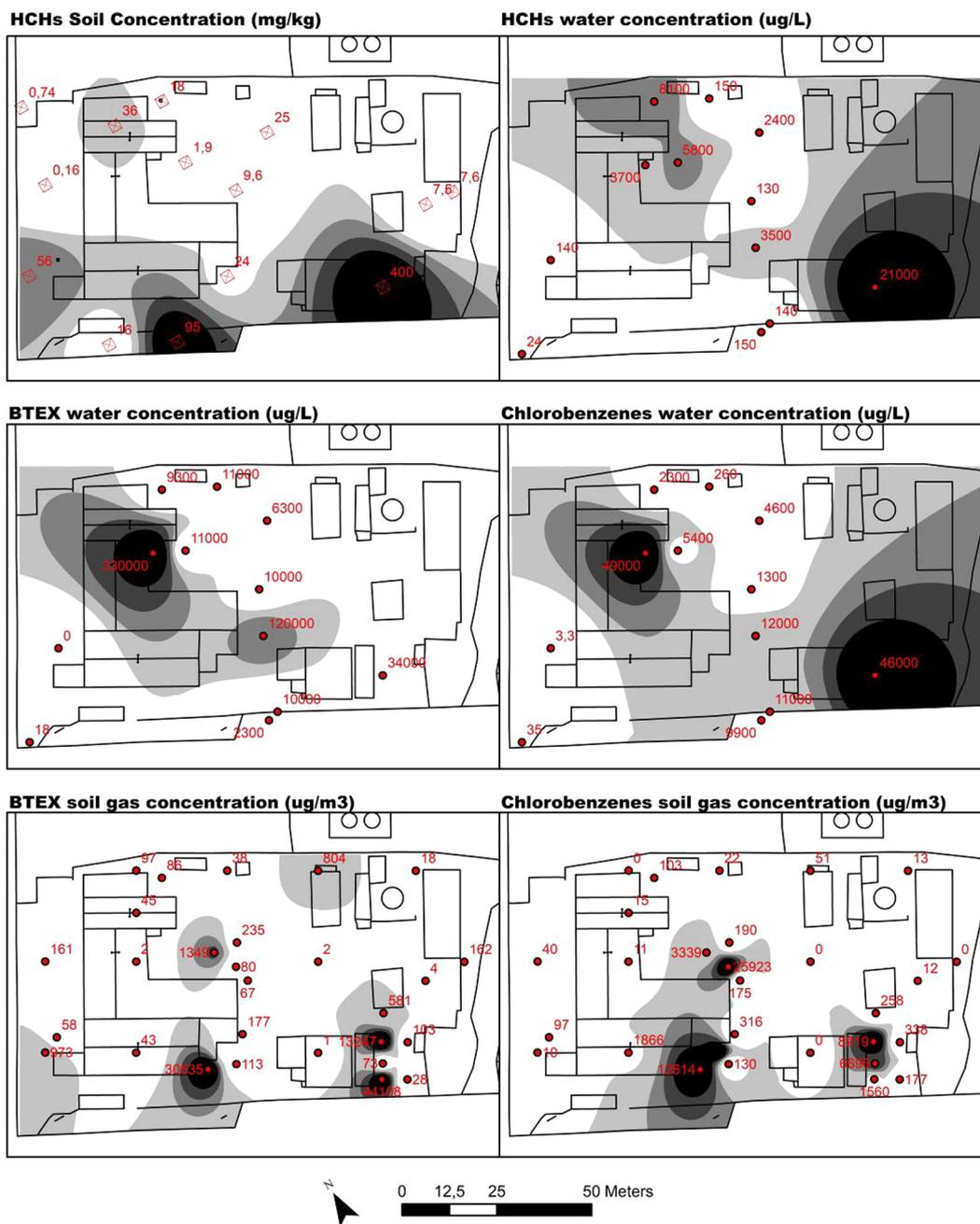


Fig. 3. Isoconcentration maps of organic compounds in soil, groundwater and soil gas samples.

between the last rain episode and the beginning of each sampling campaign. A summary of the analytical results is presented in Table 1, including the mean value and coefficient of variation (CV) obtained for field replicates. ²²²Rn-in-soil-air activities ranged between < 200 Bq/m³ and 52300 Bq/m³, with similar values of mean and standard deviation for Campaigns #1 and #2 (the sampling positions included in the third Campaign were restricted to 4, therefore mean values and standard deviations are not comparable). There is a significant negative linear correlation between the mean values of replicates and their coefficients of variation ($r = -0.75$, statistically significant at a 99% confidence level). This result indicates an increasing analytical uncertainty with decreasing ²²²Rn activity in the samples.

Inverse Distance Weighted (IDW) interpolation with a squared distance term was used in ArcGIS to produce maps of ²²²Rn concentrations at the site. IDW was chosen because its results were the most consistent with original input data in a comparison performed by Burrough (1986)

and Mathes and Rasmussen (2006) (Magesh et al., 2011).

Despite the differences in absolute values between campaigns #1 and #2, the resulting ²²²Rn interpolation maps show significant similarities in terms of their spatial trends. ²²²Rn determinations in both sampling campaigns presented relatively low values in the south-eastern region and the central zone of the sampled area. During Campaign #1 (and less evidently in Campaign #2), another, spatially smaller, local minimum of ²²²Rn concentration was detected in the north-eastern sector of the study site. In the absence of information from direct analytical determinations, the maps of ²²²Rn activity in soil air would therefore seem to indicate the presence of three different areas of high saturation of organic contaminants in the soil profile of the site: Areas I, II and III in Fig. 2.

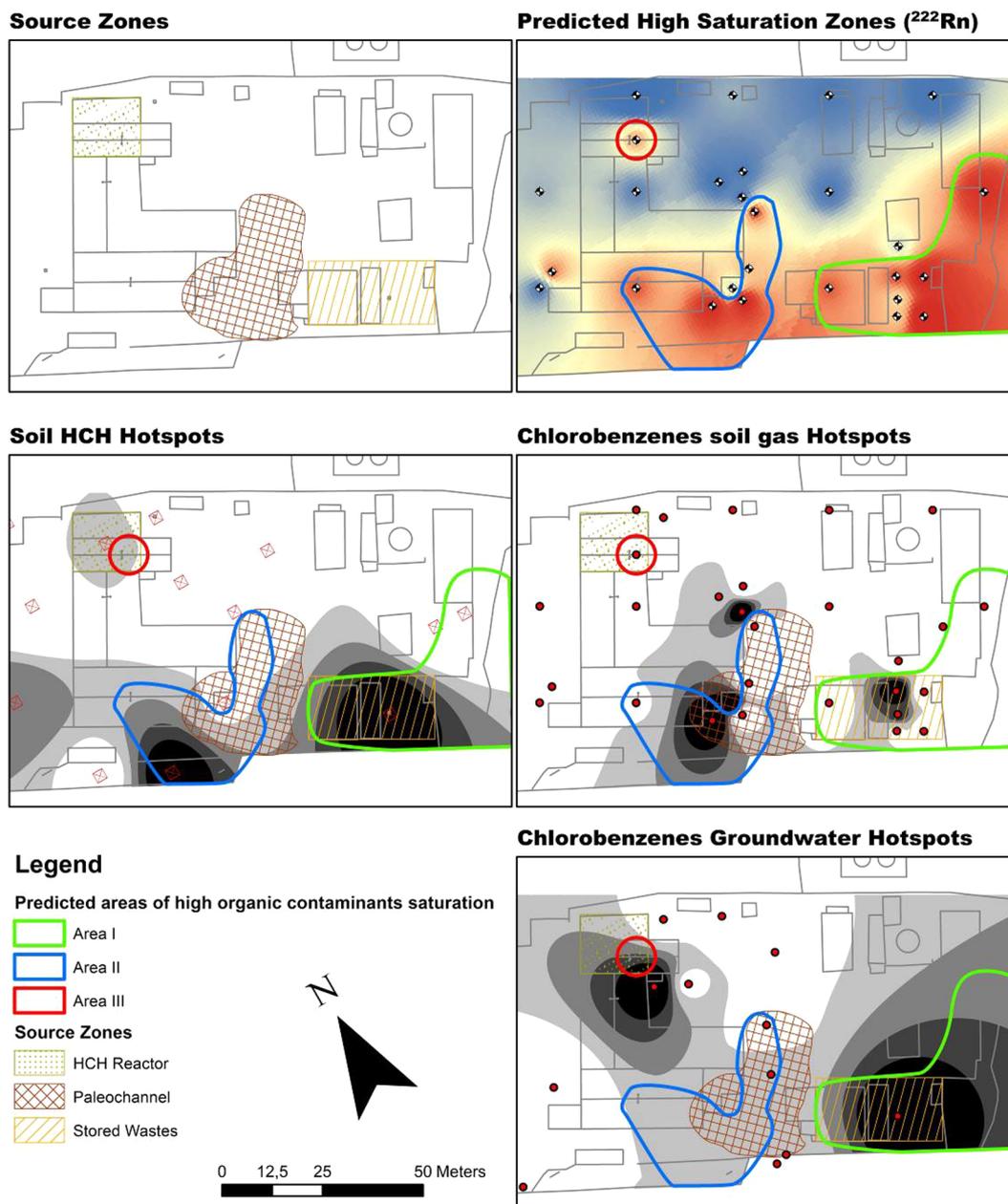


Fig. 4. Comparison of source zones, high saturation areas obtained with the ²²²Rn deficit technique, and pollution hotspots.

3.1. Comparison with direct analytical determinations.

Once the distribution of ²²²Rn activities had been represented and spatially analysed, direct analytical information was made available by regional government authorities to be used as contrast information. Specifically, the authors were provided with concentrations of benzene-toluene-ethylbenzene-xylenes (BTEX), chlorobenzenes and HCHs in groundwater from 12 monitoring wells inside the perimeter of the study area; concentrations of BTEX and chlorobenzenes in soil air from 29 soil-gas probes; and concentrations of α-, β-, γ-, δ- and ε-HCH in soil samples retrieved from 14 locations.

The top-left map in Fig. 3 shows the spatial distribution of total HCHs concentration in soil samples retrieved between 2 and 4 m.b.g.s. The highest concentrations, reaching values of 400 mg/kg, are found to the south-east, beneath the area where production wastes were stored outdoors without control. The location of this hotspot coincides remarkably well with High Saturation Area I in the map of ²²²Rn concentrations in soil air (Fig. 4).

The top-right map and the two central maps in Fig. 3 show, respectively, the surface trace of concentrations of HCHs, BTEX and Chlorobenzenes in groundwater at the site. A plume of BTEX and Chlorobenzenes is located in the northern section of the plant, where the chemical reactor was situated, and seems to reach the paleochannel, in the centre, which, given the topography of the impermeable layer of marls, probably acts as a sink of pollutants at the site. The accumulation of dissolved organic contaminants is again reflected in the spatial distribution of ²²²Rn in soil air at the site, with two minima (High Saturation Areas II and III) precisely above the paleochannel and beneath the reactor (Fig. 4). Another hotspot of dissolved HCHs and chlorobenzenes is located, as in the case of HCHs in soil, in the waste storage area to the south-east of the plant. This hotspot is accurately mirrored in High Saturation Area I in the bottom-left map (²²²Rn in soil air) in Fig. 4.

Lastly, the bottom two maps in Fig. 3 present the surface distribution of VOCs (BTEX and chlorobenzenes) in soil gas. Two maxima of the concentration in soil air of both contaminants are revealed above the

western section of the paleochannel (and also in the eastern part, in the case of chlorobenzenes) and the area of accumulation of wastes, coinciding with ^{222}Rn minima in High Saturation Areas II and I, respectively (Fig. 4).

The location of inferred hot-spots of contamination in Fig. 3 is different depending on the type of matrix analysed (soil, water or soil air). Although this circumstance may be partly explained by the low number of soil and groundwater samples available, the fact remains that, unlike the maps of ^{222}Rn concentrations in Fig. 2, none of the individual maps in Fig. 3 identify simultaneously all three areas of high saturation at the site.

4. Uncertainties and limitations.

The results of the blind test confirm that, under the right conditions, the ^{222}Rn -deficit technique is capable of detecting and delineating the surface trace of sub-surface accumulations of mixtures of organic contaminants. There is a clear spatial relationship between areas with low ^{222}Rn activity and pollution hotspots (Fig. 4). Two of the limiting factors often cited in the scientific literature, i.e. the variability of radium contents in different geological materials and the fluctuating production rate of ^{222}Rn with textural variations (Chitra et al., 2018; Cohen et al., 2016; Cothorn and Smith, 1987) do not seem to play a significant role in the texturally and compositionally homogeneous site under investigation.

However, during the course of the field blind test, other important limitations of the ^{222}Rn -deficit technique have been revealed and a discussion of their influence on the interpretation of results is presented below:

4.1. Diffusive vs. Advective flow and depth of contaminants

At the study site, the top of the soil profile is composed of quaternary materials with no evidence of significant fractures in the underlying marl formation that could promote an advective or co-advective (with carrier gases) transport of ^{222}Rn . Additionally, the surface of the premises is paved, isolating the soil from barometric fluctuations. As a consequence, diffusive transport should be the dominant mode of ^{222}Rn migration. The downward migration of contaminants stops at the top of the marl layer, which acts as an impermeable barrier, resulting in the accumulation of the complex mixture of organic chemicals at the relatively shallow depth of 2 to 4 m.b.g.s. (Fig. 1). Soil air was sampled at a depth of 0.8 m, within the diffusion length of ^{222}Rn for the quaternary materials underlying the site (Arvela et al., 2016; Sogaard-Hansen and Damkjaer, 1987), and it therefore reflects the decrease in ^{222}Rn concentration associated with subsurface accumulations of contaminants.

At other sites with a low contribution of advective transport, however, variations of ^{222}Rn concentrations in soil air would only be spatially correlated with changes in contaminant residual saturation if the depth of the sampling point falls within the maximum diffusion radius of ^{222}Rn from the source zone (Cohen et al., 2019, 2016; Schubert et al., 2001). Hence, the ^{222}Rn -deficit technique will probably be ineffective for the delineation of deep plumes of NAPLs and/or in soils with low soil air permeability and high water saturation ratios, two factors which reduce the effective diffusion of ^{222}Rn in the sub-surface environment (Arvela et al., 2016; Castelluccio et al., 2015; Prasad et al., 2012; Singh et al., 1993).

4.2. Variability of ^{222}Rn concentrations in soil air: Influence of temperature.

The variability of ^{222}Rn concentrations in soil air was evaluated through replicated measurements at four sampling positions in the three sampling campaigns. The results of these replicated

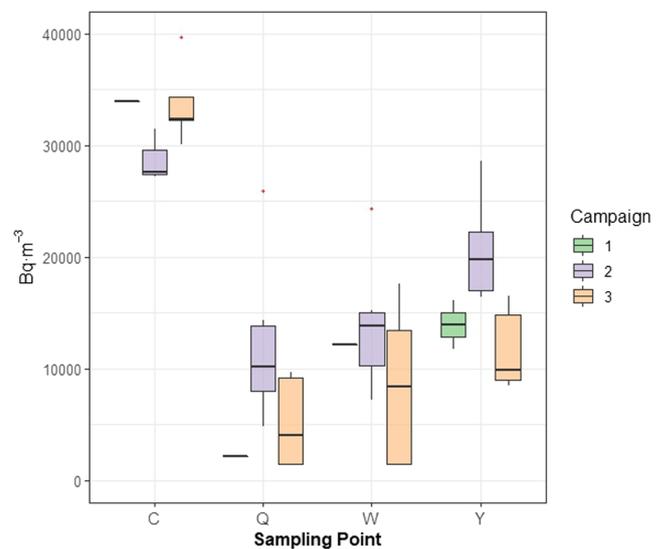


Fig. 5. Boxplot of replicated ^{222}Rn measurements during the three sampling campaigns. The lower and upper limits of the box represent the first and third quartiles of the data, respectively. The horizontal line inside the box represents the median. Vertical lines extend from the first and third quartiles to data between -1.5 and $+1.5$ times the interquartile range. Outliers (data exceeding 1.5 times the interquartile range) are represented as red dots.

measurements are represented in Fig. 5.

As discussed in the previous section, the variability of replicated ^{222}Rn measurements at the same point is probably not a consequence of changes of atmospheric pressure, given the characteristics of the site and the sampling depth. Other meteorological parameters could instead explain the observed variability, such as the diurnal temperature gradient, that could cause a decrease in the ^{222}Rn concentration in the upper soil profile (down to a depth of 2 m) during the evening and an increase during the night and early morning due to its effect on the transport rate (Schubert, 2015; Schubert and Schultz, 2002). The influence of this diurnal thermal variation is assessed in Fig. 6, where ^{222}Rn concentration in soil air at four sampling points and temperature data obtained during field campaign #3 are jointly plotted.

A Spearman correlation analysis (Table 2) indicates a statistically significant correlation between the variation of ^{222}Rn measurements and air temperature at ground level, a fact that has also been noted by other authors (Yang et al., 2019). Fig. 6 also shows that diurnal changes of concentration of ^{222}Rn in soil air at different points follow the same pattern, gradually increasing until the early afternoon and slowly decreasing after then.

The concentration of ^{222}Rn in soil air can vary by more than 10000 Bq/m³ between a measurement in the early morning and a measurement at the same point after the moment of maximum insolation, a fact that can distort the maps of iso-concentrations of ^{222}Rn in soil air if isolated measurements taken at different times in different sampling points are plotted together.

The influence of this confounding factor can be minimized by averaging the individual concentrations registered at each sampling point (replicates) during a day-long campaign and using those averages to draw the iso-concentration maps and to infer the location of high saturation areas. The interpolation maps of average values in Fig. 2 (top-left and both bottom maps) demonstrate that this approach results in stable (i.e. invariant enough) spatial representations whose interpretation is consistent with independent results of other direct and indirect characterization techniques.

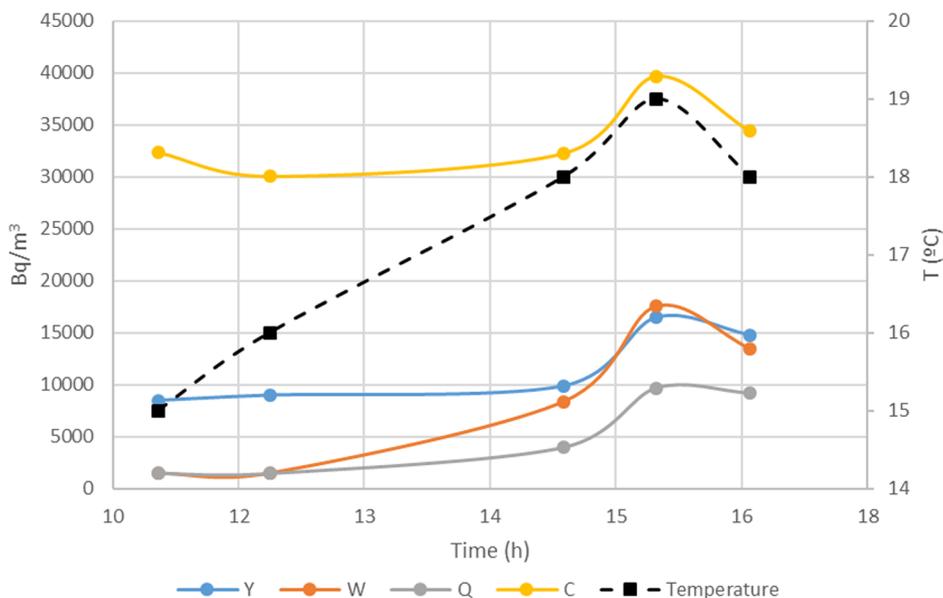


Fig. 6. Diurnal variation of ²²²Rn signal and atmospheric temperature.

Table 2

Spearman correlation analysis of ²²²Rn and atmospheric temperature during field Campaign #3. Statistical significance code: 0 ‘****’ 0.001 ‘***’ 0.01 ‘**’ 0.05 ‘.’ 0.1 ‘.’ 1.

	Temperature	Y	W	Q	C
Temperature	1.00	**	*	*	
Y	0.97	1.00	**	**	
W	0.95	0.97	1.00	***	.
Q	0.95	0.97	1.00	1.00	.
C	0.62	0.70	0.82	0.82	1.00

5. Conclusions

Although direct knowledge (through drilling and soil and groundwater sampling and analysis) of the nature and concentrations of pollutants in the subsoil of the site is not exhaustive, the results of the ²²²Rn-deficit technique in terms of the location of hot spots coincide with those obtained using standard direct and indirect prospecting techniques and are coherent with the situation of historical sources of pollution and with the characteristics of the geologic materials underlying the installation.

Compared to standard indirect assessment techniques (i.e. soil gas), which provide information on only one individual type of contaminants, the ²²²Rn-deficit technique seems to be capable of delineating NAPL lenses and areas with high residual concentrations in the vadose zone of not only volatile but also non-volatile organic substances. If the comparison is made against the performance of conventional investigation tools (i.e. drilling and soil groundwater sampling and analysis), measurements of ²²²Rn in soil air are obtained in quasi-real time, with a much higher spatial density than that of intrusive techniques, at a much faster rate (136 independent determinations in 5 days) and at a significantly lower cost.

While the ²²²Rn-deficit technique has proven its potential to be an efficient tool for the preliminary assessment of sites contaminated with complex mixtures of organic contaminants, its applicability is limited by two factors: Firstly, at sites where geological conditions do not promote advective transport of ²²²Rn, the depth of investigation is determined by the distance between the inlet point of the sampling probe and the location of the contaminated material, which should be

less than the diffusion length of ²²²Rn. For standard sampling depths (between 0.5 and 1 m) the applicability of the ²²²Rn-deficit technique would be limited to the first 3–4 m of the soil profile. Secondly, the concentration of ²²²Rn in soil air changes at each sampling point with diurnal temperature variations. The uncertainty that this fact introduces in the delineation of subsurface accumulations of contaminants can be minimized by using the average of replicated measurements throughout the workday in each sampling location.

CRediT authorship contribution statement

E. De Miguel: Conceptualization, Methodology, Project administration, Funding acquisition, Supervision, Writing - review & editing. F. Barrio-Parra: Conceptualization, Methodology, Formal analysis, Data curation, Writing - original draft. M. Izquierdo-Díaz: Investigation, Data curation. J. Fernández: Methodology, Resources. J.E. García-González: Investigation, Resources. R. Álvarez: Investigation, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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