British Geological Survey
NATURAL ENVIRONMENT RESEARCH COUNCIL

D20 Report: Soil Gas surveys in the Weyburn oil field (2001-2003)

Sustainable Energy and Geophysical Surveys Programme

Commissioned Report CR/04/030N

BRITISH GEOLOGICAL SURVEY

COMMISSIONED REPORT CR/04/030N

D20 Report: Soil Gas surveys in the Weyburn oil field (2001-2003)

S. Beaubien, M. H. Strutt, D. G. Jones, J.-C. Baubron, C. Cardellini, S Lombardi, F. Quattrochi and L. Penner

Key words

Soil gas, CO_2, Weyburn.

Front cover

Cover picture details, Soil gas measurement at the Weyburn oil field.

Bibliographical reference

S. BEAUBIEN, M H STRUTT, D G JONES, J-C BAUBRON, C CARDELLINI, S LOMBARDI, F QUATTROCHI AND L PENNER. 2003. D20 Report: Soil Gas surveys in the Weyburn oil field (2001-2003). *British Geological Survey Commisioned Report*, CR/04/030N. 62pp.

Keyworth, Nottingham British Geological Survey 2004

BRITISH GEOLOGICAL SURVEY

The full range of Survey publications is available from the BGS Sales Desks at Nottingham and Edinburgh; see contact details below or shop online at www.thebgs.co.uk

The London Information Office maintains a reference collection of BGS publications including maps for consultation.

The Survey publishes an annual catalogue of its maps and other publications; this catalogue is available from any of the BGS Sales Desks.

The British Geological Survey carries out the geological survey of Great Britain and Northern Ireland (the latter as an agency service for the government of Northern Ireland), and of the surrounding continental shelf, as well as its basic research projects. It also undertakes programmes of British technical aid in geology in developing countries as arranged by the Department for International Development and other agencies.

The British Geological Survey is a component body of the Natural Environment Research Council.

Keyworth, Nottingham NG12 5GG

☎ 0115-936 3241 Fax 0115-936 3488
e-mail: sales@bgs.ac.uk
www.bgs.ac.uk
Shop online at: www.thebgs.co.uk

Murchison House, West Mains Road, Edinburgh EH9 3LA

☎ 0131-667 1000 Fax 0131-668 2683
e-mail: scotsales@bgs.ac.uk

London Information Office at the Natural History Museum (Earth Galleries), Exhibition Road, South Kensington, London SW7 2DE

☎ 020-7589 4090 Fax 020-7584 8270
☎ 020-7942 5344/45 email: bgslondon@bgs.ac.uk

Forde House, Park Five Business Centre, Harrier Way, Sowton, Exeter, Devon EX2 7HU

☎ 01392-445271 Fax 01392-445371

Geological Survey of Northern Ireland, 20 College Gardens, Belfast BT9 6BS

☎ 028-9066 6595 Fax 028-9066 2835

Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB

☎ 01491-838800 Fax 01491-692345

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon, Wiltshire SN2 1EU

☎ 01793-411500 Fax 01793-411501
www.nerc.ac.uk

Foreword

This report describes soil gas monitoring carried out in and around the Phase A1 injection area of the Weyburn Oilfield over the period July 2001 to September 2003. It covers the main soil gas studies at Weyburn undertaken with European Commission funding under the EU 5th Framework Programme and additional soil gas studies funded through the Petroleum Technology Research Centre in Calgary, Canada. The investigations were carried out by the British Geological Survey (D G Jones, M H Strutt), the University of Rome La Sapienza (S Beaubien, S Lombardi) and Instituto Nazionale di Geofisica e Vulcanologia (C Cardellini, F Quattrochi) from Italy, and the Bureau de Recherches Géologiques et Minières (J-C Baubron) from France with assistance from J D Mollard and Associates (L Penner) from Canada.

Acknowledgements

The authors would like to thank the many staff of Encana who helped the fieldwork go smoothly, organised land access and surveying and provided field support. In particular we would like to acknowledge the invaluable assistance provided by Ken Ferguson. All the sites were surveyed by Condon Surveying Group, with special thanks to Lowell Peterson

Contents

FIGURES

TABLES

Summary

The International Energy Agency (IEA) Weyburn project is an international project that is studying the feasibility of long-term geological storage of carbon dioxide (CO_2), allied to an enhanced oil recovery operation, by Encana, in the Weyburn oilfield, south-eastern Saskatchewan, Canada. CO_2 is being injected into the oil reservoir to improve oil production, whilst at the same time the process should lead to long term geological storage of large volumes of CO_2. Soil gas studies are being undertaken as part of an EU-funded component of this project, with the primary objectives of measuring the natural background concentrations and to ascertain if there is a leak of CO_2, or associated tracer gases, as a direct result of the solvent flood presently occurring at the Encana Weyburn oil field. This report describes the results from three sampling periods conducted between July of 2001 and October of 2003.

Sampling of the large 360 point grid above the injection area over the last three years showed CO_2, O_2 and CO_2 flux values in the range of natural soils, and these observed levels can be explained by standard metabolic pathways that normally occur in the shallow soil horizon. The spatial anomaly distributions of these gases are reasonably reproducible from year to year and season to season, despite the fact that the range of values vary from high concentrations in the hot wet summer of 2001 to the low values found in the fall of 2002 and 2003. In contrast to these biologically active species, the statistical and spatial distribution of radon and thoron is very similar from one sampling season to the next. This provides support for the idea that leakage is not taking place, as one would expect to see high radon during the periods of high CO_2 if the latter was acting as carrier for the more trace former gas. Hydrocarbon values were found to be within normal ranges in October of 2003, however the previous two seasons showed elevated values which were not fully expected. In fact ethylene and propane show a statistical distribution over the three years which is quite similar to that of CO_2, whereas methane and ethane have relatively constant values except for more concentrated outliers during the first and second seasons. As the heavier hydrocarbons do not normally originate via shallow biological reactions it is difficult to reconcile these results with those of the other gases.

A comparison of the grid data with that of the background site, located in similar surface geology but outside the Weyburn oil field, shows a very similar statistical distribution for all monitored parameters. This result supports the interpretation that the observed gas concentrations are not due to deep leakage. In particular, both sites have a very similar CH_4 / (C_2H_6 + C_3H_8) ratio. This value is low and in the range of thermo-catalytic regime, however the fact that such a value was found both within and outside the oil field implies that the origin of these gases are not necessarily from a deep oil reservoir.

Highly detailed horizontal profiles performed across radon and CO_2 anomalies defined during the first year sampling of the main grid were used both to select sites for the installation of the long term radon monitoring probes, as well as to study in detail the elevated soil gas concentrations and to relate them to surface lineaments. The work conducted on these profiles showed reproducible trends for CO_2, CO_2 flux and, to a lesser extent, radon, with anomalies occurring in correspondence with low lying areas and surface water. Although some of these coincide with mapped lineaments, which could in theory be the surface expression of deep faults, it is perhaps more likely that these lineaments are shallow features that accumulate water and nutrients and thus produce biologically created anomalies.

Finally work was also performed on a number of sites which could represent possible vertical migration pathways, including two decommissioned wells, a river lineament and a salt collapse structure with its associated faulting. Sampling over these areas showed very little in the way of clear indications of deep gas leakage. Data from the salt collapse structure was extremely low. Results from the river lineament gave a clear CO_2 anomaly in the valley and an increasing He trend in the area of the river; the former was interpreted as being of a shallow origin while the

latter is presently not fully understood. Finally the values obtained around the former oil wells were within the range of values observed over the main grid, although the CO_2 median from one site was slightly higher.

Overall, there is no evidence so far for escape of injected CO_2 from depth. Further monitoring of soil gases is necessary to verify that this is the case in future and more detailed work is required to better understand the causes of variation in soil gas contents, and investigate further, possible conduits for gas escape.

1. Introduction

This report describes soil gas concentration and flux monitoring carried out in October 2003 in and around the Phase A1 injection area of the Weyburn Oilfield, and compares these results with the data collected during the previous 2 years of the project. The bulk of this work was undertaken within the framework of the present EC project, but a contribution also came from the Petroleum Technology Research Centre (PTRC, Regina, Canada) for the sampling of some specific sites; both data sets have been integrated here to allow for a better interpretation of the studied system. The objectives of this work, which was performed by the British Geological Survey, the Università di Roma ‘La Sapienza’ and the Instituto Nazionale di Geofisica e Vulcanologia from Italy, and the Bureau de Recherches Géologiques et Minières from France, are to:

- Establish baseline soil gas values using grid sampling and profiles, and to compare these results with future datasets
- Evaluate natural variations in soil gas including seasonal effects
- Understand geochemical reactions and gas flow pathways in geological sequences
- Identify sites of higher gas flux that may be indicative of deep gas escape
- Enable long term monitoring to evaluate possible escape of injected CO_2
- Address possible public concerns over geological storage of CO_2

Three principal techniques were used to address these questions, including the analysis of the concentrations of various gas species in the pore spaces of the shallow unsaturated soil horizon (‘soil gas’), the measurement of the mass transfer rate of CO_2 across the soil-atmosphere interface (‘gas flux’) and the long-term monitoring of radon flow rates, as a proxy for CO_2, using probes buried for up to a year at 2 m depth in the soil (‘Rn probes’). Clearly the gas of principal interest for the goals of this project is CO_2, due to the fact that it is being injected in large quantities into the underlying deep oil reservoir and due to concern that it might eventually migrate to surface. However CO_2 is highly soluble and can be consumed via acid-base reactions, and thus its movement (if any) might be attenuated during the short period of the present monitoring. Furthermore the interpretation of CO_2 data is complicated by the fact that this gas is involved in metabolic reactions, both via soil microbes as well as plant roots. Because of these possible sources and sinks of CO_2 a large suite of other soil gas species were analysed which might help define possible flow paths that CO_2 may follow in the future or help resolve the origin of the present CO_2 anomalies; these include less reactive gases associated with the reservoir which could be used as tracers of deep flow (e.g. He, Rn and CH_4) and gases that might be involved in shallow biological reactions (e.g. O_2, CH_4 and C_2H_4).

Work reported here comprises three years of soil gas and gas flux results from the main grid above the Phase A1 CO_2 injection area (hereafter referred to as the ‘main grid’), and the 6 detailed horizontal profiles and 6 vertical profiles conducted within the area of the main grid. Results are also presented for 7 small additional sites which were added, with the help of PTRC, to address issues that had arisen during work on the main grid over the previous two years. The first issue involves the need to better understand the background soil gas concentrations in the agricultural fields of this part of southern Saskatchewan, without the added complication of 50 years of oil-field infrastructure and the ongoing CO_2 flood (accepting that it is difficult to completely get away from oil wells in this area). To address this a small background site was chosen about 10 km to the north-west of the main grid which has a similar topography, soil types and vegetative cover. The second issue regards specific man-made or natural vertical structures which may act as conduits for upwardly migrating gases, such as the injected CO_2. Three sites were thus selected on the basis of geological and infrastructure considerations for more detailed sampling, including decommissioned wells (two small sampling grids), a river lineament which may represent the surface expression of a deep fault (two horizontal profiles) and a salt collapse structure at depth which shows vertical faulting in seismic sections (two horizontal profiles). The location of each site is presented in Figure 1 a and b along with a brief description in Table 1.

2. Methods

2.1. SOIL GAS COLLECTION AND ANALYSIS

Soil gas samples were collected over regular grids, along horizontal profiles and along vertical profiles at individual locations (Figure 1 a and b). Sampling points for soil-gas surveys are normally selected on the basis of required sampling density, ease of access to the location and suitability (such as level of soil saturation). Another extremely important factor at the Weyburn site is the extensive underground infrastructure that occurs throughout the area, including buried oil, gas and water pipelines, electrical cables and telephone lines. As such the sites were chosen in consultation with Encana personnel and the agreed upon points were geophysically surveyed for buried structures and located with GPS by Condon Surveying. If buried objects were found, the point was moved within a radius of 50m.

The probe used to collect soil gas samples consisted of a modified 6.4mm (¼ inch), thick-walled, stainless-steel tube onto which two steel cylinders were welded to act as pounding surfaces when installing and removing the probe with a co-axial hammer. The bottom end of the probe was fitted with a sacrificial tip to keep the tube clean during pounding into the ground, whereas the top end was left free so that a septum holder or silicone tubing could be attached for collecting gas samples.

The standard sampling procedure (Ciotoli et al., 1999; Ciotoli et al., 1998) involved pounding the probe to a depth that is not influenced by the input of atmospheric gases via diffusion or barometric pumping (Hinkle, 1994); at Weyburn this was determined to be between 60 and 90 cm below ground surface on the basis of vertical profiling. A small hand pump was then attached to the upper end and evacuated, and then the probe was gently tapped upwards in order to dislodge the sacrificial tip. Once the bottom of the probe was free of the tip and within a gas permeable horizon the hand pump would fill with air, thereby indicating that it was possible to sample. The hand pump was then pumped twice to clean the probe of any atmospheric air, a septum holder was attached to the open end of the tube, the needle of a 60ml plastic syringe was inserted through the septum and a 60ml gas sample was drawn up and injected into a previously evacuated stainless steel container. These containers were then transported back to the laboratory and analysed for hydrocarbon species (C1-C3 alkanes and C_2H_4), sulphur species (COS and SO_2) and permanent gases (N_2, O_2 and CO_2) using two Fisons 8000-series bench gas chromatographs, as well as He using a Varian helium leak detector. After the septum holder was removed gas was pumped via a bellows pump into a Pylon AB5 radon monitor for the analysis of radon and thoron, and then the probe was attached to a Infrared gas analyser (Geotechnical Instruments GA1.1 or ADC LFG20) for the measurement of CO_2 and O_2 directly in the field. A number of sites (mostly the seven additional sites, rather than the main grid and profiles) were also sampled for He and Rn using other techniques. He was studied by filling a 1L Teflon bag with soil gas and analysing the sample the same day using a Alcatel 100HDS Helium mass spectrometer with a sensitivity of +/- 0.01 ppm; this He data was normalised to atmospheric air concentration (5.24 ppm) at local pressure between each sample. Results were verified using gas standards before and after the field campaign. Rn was also measured in the field laboratory (without Tn) using 125 ml ZnS scintillating bottles and a Calen counting chain (F-Algade) with a 10 minute accumulation time after 3 hours delay for equilibrium of Rn daughters and decay of thoron products. With such conditions, Rn accuracy of sampling and measurement is usually better than 10%.

The approach used for the vertical profiles involved the use of a long probe with lateral sampling ports and a sharp pointed lower end, instead of the sacrificial tip. This probe was progressively pounded to different depths (typically 25 to 30 cm apart), the probe was cleaned of atmospheric air as described above and then the sample was taken. If gas flow was not possible at a certain depth the probe was either pounded deeper in the hope of penetrating through an impermeable layer, or the profile was abandoned. In order to maximise depth penetration at some locations, 30cm of soil was removed from around the probe when it had been hammered to its maximum depth, and it was then pounded to this new depth. By repeating this procedure at one site it was possible to sample to a maximum depth of 1.8 m.

2.2. CO_2 FLUX MEASUREMENTS

The flux of CO_2 at the soil-atmosphere interface was measured using the accumulation chamber technique, as described in detail in Chiodini et al., 1995, 1998, 1999 and 2000. The gas analyser used for the two surveys was the IRGA LI-COR 800 equipped with the optical bench (LI-COR 800-905) set to work in the range 0-5000 ppm of CO_2. The gridded data have been used to create CO_2 flux maps and to estimate the total amount of CO_2 emitted by the surveyed areas.

2.3. GAMMA SPECTROMETRY

Gamma spectrometry was carried out at the Minard’s background site and part of the main grid area. This technique measures U and Th series radionuclides (as well as K and total gamma) and hence there is a link to radon and thoron measurements. There can be a coincidence between anomalies of these gases and gamma anomalies, for example where structures, such as faults, are associated with gas escape. The instrument (an Exploranium GR320 with 76 x 76 mm NaI(Tl) detector) can be operated in static mode, or continuous measurements taken while the operator walks slowly across the ground. Positioning in continuous mode was obtained using a handheld GPS receiver (with an accuracy of a few m). In this mode there is the potential to detect features missed by point gas sampling. Both styles of operation were used on the main grid, but only continuous traverses at the background site. Lack of access to the other sites, when this instrument was being deployed, prevented further work being carried out.

Comparison was made between the main grid and the background site to evaluate whether the soil compositions were similar, and thus soil gas comparisons between the two appropriate. Gas escape can also alter the K, U and Th concentrations of the surface soil leading to anomalies that may indicate areas of leakage from depth (e.g. Klusman, 1993; Tedesco, 1995; Schumacher and Abrams, 1996; Schuamcher and LeSchack, 2002).

2.4. CONTINUOUS ^{222}RN MONITORING

Electronic Rn sensors with internal memory (Algade Barasol probes) were installed at six sites in September 2001 and data have been recorded for extended periods since then. The sites were selected from the detailed soil gas profiles located across Rn and CO_2 anomalies seen in the initial main grid data. Detailed Rn, Tn, CO_2 and He measurements were made around specific anomalies and radon probe sites chosen that reflected potential deep gas escape (He anomalies, higher Rn) as well as ‘background’ sites for comparison. The clearest anomalies on traverses A and B were chosen , all having similar soil and crop types (mainly wheat).

The probes were installed in holes up to 1.9m deep, lined with plastic pipe the top of which was sunk about 40cm below the ground surface. Once in place the pipe was covered by Goretex® waterproof, but gas permeable, membrane and covered with soil. This allows the soil gas to flow freely to atmosphere. The instrument will record data for up to a year, which is downloaded after retrieval of the probe. After downloading and replenishment of the batteries the probe is reinstalled and recording continued. Measurements were made every hour of Rn concentration, temperature and atmospheric pressure. The data can be modelled to provide information on gas transport mechanisms (diffusion, advection) and rates. They show seasonal variations in Rn concentrations, which can be modelled against atmospheric parameters, indicating the influence of other factors on gas migration. Moreover, CO_2 fluxes deeper in the soil can be calculated and compared to surface rates. Ultimately they may reveal possible modifications of the gas transfer pressure conditions constraining the gas velocity, eventually with a contribution from the reservoir. They could then detect the very first precursors of a possible CO_2 escape.

2.5. DATA PROCESSING

All the soil gas and gas flux data was first examined statistically using the software packages Statistica (Statsoft), Microsoft Excel and S-Plus. This approach allowed a rigorous comparison between the various data sets in order to define trends or anomalous distributions. This was mainly accomplished through the use of normal-probability plots (NPP) and box-whisker plots (BWP). An NPP, created by plotting observed residuals versus observed concentration values, is used to evaluate whether and to what extent the distribution of a variable follows a normal distribution (Sinclair, 1991). If the data is normally distributed then all values should fall onto a straight line, however if the data is not normal then flexure points between linear segments can be used to define sub-populations which may be the result of different origins, controlling mechanisms or transport pathways. The NPPs were mainly used to interpret the large data set from the main grid, and then the resulting population boundaries were used to subdivide and plot (i.e. contour map colour scales) all the other data sets. This approach allows for a more objective, easier comparison between both detailed and regional sites. An example of the NPP procedure followed to define the various populations is given in Figure 2 for the main grid's 2003 CO_2 values. In contrast to the NPPs, BWPs are very useful for the visual comparison of entire data sets. These plots, which can be used to compare the statistical distribution of a single gas from different sites or from the same site at different times, consist of a central line marking the median concentration, box extremes marking the upper and lower quartiles, 'whisker' extremes marking the normally distributed maximum and minimum values, and individual symbols showing outlier values. In addition to the statistical processing of the data, all results were plotted using the software packages Surfer or ArcView for the gridded data, and Grapher, S-Plus or Excel for the horizontal profile results.

3. Results

3.1. DATA INTERCOMPARISONS AND QUALITY CONTROL TESTS

A comparison between the CO_2 data from the field infrared analyses and the gas chromatograph measurements conducted in the lab (Figure 3a) show a slope very close to unity (1.03) and good agreement between the two data sets (r^2 = 0.92). These results provide quality control for the integrity of the stainless steel sample containers, as significant discrepancies could indicate faulty canisters thus allowing the data from such samples to be treated with caution. The correlation also demonstrates the validity of the infrared analyses and indicates that it would be appropriate to use the field measurements to select areas for more detailed study during a field campaign.

The two sets of Rn measurements, one conducted immediately in the field and the other performed three hours later after equilibration, do not correlate as well as the CO_2 data (Figure 3b). The field Pylon measurements provide data for Tn as well as Rn and involve shorter counting times. They are likely to have lower precision than the longer counts for Rn alone, but are suitable as a rapid method providing almost instant results. The relationship between the two Rn datasets is being investigated further. Due to the rapid nature of the field-based Rn measurements, far more data was collected using this technique and thus these results are discussed in more detail below.

3.2. GRID OVER THE PHASE A1 INJECTION AREA

The main soil gas and gas flux grid was first established in 2001 (Figure 1 a and b) as a way to monitor for the possible leakage of injected CO_2 to surface. At that time 75% of the sampling points were above the Phase A1 CO_2 injection area while the remaining points were outside. Although the CO_2 injection area has increased during subsequent phases it has not been possible, for logistical reasons, to expand the main soil gas sampling grid to encompass these new areas. The grid itself is 3.6 x 4.0 km in size, has a sample spacing of approximately 200m and consists of 360 individual sampling points. It has been sampled all three years for a complete suite of field- and laboratory-based soil gas analyses as well as the measurement of CO_2 soil-to-atmosphere flux.

3.2.1 Statistical Variations

Box and whisker plots (see 'Data Processing' above) given in Figure 4 show the statistical distribution of gas flux and soil gas concentrations for the main grid for each of the three years of the project. From this figure it is quite evident that the flux (a) and soil gas concentration (b) of CO_2 decreases markedly from the sampling conducted in July of 2001 to September-October of 2003. Not only do the bulk of the samples (i.e. between the upper and lower quartiles) become progressively lower but also the spread and level of outlier samples becomes more reduced and compact. As the sampling campaigns occurred during progressively dryer and cooler soil conditions one can hypothesize that the observed values may be due to shallow biological reactions that produce CO_2 as a metabolic by-product. This important point will be discussed in more detail below.

In sharp contrast to the behaviour of CO_2, the radioactive gases radon and thoron show a relatively stable distribution for all three years. These gases were studied primarily because they have a short half life (e.g. 3.5 days for Rn) and thus the occurrence of a significant anomaly may indicate transport of deep radon facilitated by a carrier stream of CO_2 advecting upwards along a highly permeable pathway, like a fault (Lombardi et al., 1993, Lombardi et al., 1996). Instead the relatively constant distribution of these phases during periods when the CO_2 concentration and flux is successively reduced, implies that these gases have a shallow in-situ origin. Only the data from 2001 is slightly reduced with respect to the other years, however this may be due to an analytical artefact because two different instruments (an EDA 200 and Pylon AB5) were used the first year while only the Pylon was used for the following two.

The temporal variation of CH_4 (e) is different. Although there is a decrease in outlier values with each successive campaign, there also appears to be a slight increase in the median (0.7 to 1.1 ppm) and quartile values over the same period. This trend may be due to the seasonal drying of the soil and subsequent increase in soil air permeability, resulting in greater downward diffusion of atmospheric air with its constant methane concentration of approximately 2.5 ppm. The distribution of C_2H_6 (f) is similar to that of CH_4, although the difference from year to year with respect to outliers is far more pronounced while the distribution of the bulk of the samples is more constant.

Finally the variations in C_2H_4 (g) and C_3H_8 (h) are very similar to those of CO_2 and CO_2 flux, with both the outliers and bulk of the samples decreasing markedly from year to year during each successively later season. This too implies a shallow biological origin for these gases. As the correlation between soil gas CO_2 and these two hydrocarbons is very low, however, it is likely that they are produced via different metabolic pathways.

3.2.2 Spatial Variations

The spatial variations of the same parameters described above can be seen in the contour maps presented in Figures 5-8. The colour scales for each contour map were defined on the basis on natural breaks observed in normal probability plots of each data set, as described above in the methods section.

The distributions of CO_2 and CO_2 flux given in Figure 5 show a similar pattern for both parameters, as might be expected, and a good correlation for each from year to year and season to season. The majority of the spot anomalies are located within section 13, the northern half of 12 and the southern half of 18 (see Figure 1b for locations), areas which have extensive ephemeral surface-water bodies. Some of these water bodies are elongated and were mapped as surface lineaments in a separate air-photo interpretation study (Mollard and Associates, Regina). Although one interpretation of these features was that they may represent the surface expression of deep faults, present data appears to indicate that the elevated values in these areas are more likely due to shallow biological reactions in the moist, organic rich soil (see discussion below). As can be seen there is no clear correspondence between the soil gas CO_2 anomalies and the location of the CO_2 injection wells (see Figure 1b).

The distribution of radon and thoron anomalies (Figure 6) are quite 'spotty', and there are no clear elongated trends which might indicate the presence of a gas permeable fault or fracture system. Although radon has much fewer anomalies than CO_2 a close comparison of these two maps indicates that most of the high radon values correspond with CO_2 highs, although there are also many CO_2 anomalies which do not have a matching radon anomaly. The distribution of thoron, on the other hand, is different from both of these gases, with many anomalies occurring in section 7 and the northern part of 18.

The hydrocarbon gases presented in Figures 7 an 8 (C_2H_4 and C_3H_8) show a very good correlation amongst themselves for a given year, however the year to year distributions for a single gas are not very similar. That said there is slightly more correlation between the 2001 and 2002 data sets, particularly for the clear anomaly seen in the SW part of section 7. Although one possible explanation for the highly variable concentrations and distributions observed in the hydrocarbon species may be a pulsed release of deep gases from the reservoir it appears more likely that they are the result of a complex interaction between shallow stratigraphy, biota, temperature, moisture content, root type and vegetative cover.

3.3. HORIZONTAL PROFILES

Data from the main regional grid was used to select 6 detailed horizontal profiles (A to F) across both CO_2 and Rn anomalies (see Figure 1b for locations). These profiles were generally 1000 to 1250 metres long and had a sample spacing of 25m in order to provide more detail than was possible in the main grid (200m spacing). Unlike the main grid, not all of the horizontal profiles were sampled each year, nor was each sample location analysed for a complete suite of measurements. Instead sampling and analysis were decided on logistical grounds, including time and equipment availability. All the graphs described below were plotted using a constant scale for each given gas type in order to better compare the results from the various profiles.

Horizontal profile A was examined each of the three years for field measured CO_2, O_2, radon and thoron, as well as CO_2 flux two years and helium (part only) one year (Figure 9). The most obvious correlation amongst these parameters is the matching of positive peaks for CO_2 (b) and negative peaks for O_2 (c) which occur on either side of the 800 m marker. This relationship implies a biological reaction which consumes oxygen and produces carbon dioxide. Interestingly there does not appear to be a strong correlation between soil gas CO_2 concentrations and CO_2 flux (a), except perhaps for the two small peaks which occur on either side of the 1200m marker. The lack of a flux peak where a concentration peak exists (such as at 800m) can be explained by an impermeable surface layer that promotes accumulation but prevents mass transfer to the atmosphere. The reverse situation (such as occurs around 100m) is more difficult to explain, however it may imply that the observed CO_2 flux has a very shallow origin, i.e. less than the penetration depth of the soil gas probe. In any case all these species show the largest peak values during the summer of 2001, in agreement with the results observed for the grid data. With regard to radon (e) and thoron (f), both gases appear to have a minor peak around 1200m which may correspond with those described for CO_2 and CO_2 flux. The only other clear feature is a small peak around 200m in the thoron plot. Helium (g) does not show any anomalous values on this profile. Note that a statistical comparison of the 2003 data from each site monitored during this campaign (Figure 10) shows that horizontal profile A has an anomalous population distribution for CO_2, CO_2 flux, radon and ethane when compared to the main grid data set. This is due to the bias introduced by sampling in an area of anomalous concentrations chosen from the grid survey of 2001, where the higher values appear to be associated with surface water and peripheral marshy vegetation.

Horizontal profile B was examined using a complete suite of analyses in 2002 and 2003, while in 2001 field analyses of CO_2, O_2, Rn, Tn and CO_2 flux measurements were made (Fig 11). As observed in HP-A there is a clear correlation between soil gas CO_2 (b) and O_2 (c), with the location of the various peaks being quite reproducible from year to year. It is interesting to note that while O_2 concentrations decrease, the distribution of N_2 (d) is quite constant across the entire profile. If the observed CO_2 peaks were due to the ascent of deep gases one would expect to see a comparable dilution of both of the other two major gases – the decrease observed only in O_2 indicates that the CO_2 peaks are likely due to biological processes. This interpretation is supported by the fact that all of the CO_2 peaks correspond with low-lying swampy ground, as outlined by plotting the data spatially on the corresponding air photo (not shown). In contrast to HP-A there appears to be a reasonably good correlation between soil gas CO_2 (b) and CO_2 flux (a), especially in the interval between metres 200 and 800. However there is no such correlation between CO_2 and the hydrocarbon gases (e, f, g and h). There is an excellent correlation, though, amongst the heavier three hydrocarbons, with distinct peaks observed around 800, 1200 and 1500 m in the 2002 data. In contrast the 2003 data is low and featureless for C_2H_4 and C_3H_8, whereas CH_4 and C_2H_6 show a higher average value across the entire profile (see discussion above regarding air permeability). Radon (i) shows a good correlation with soil gas CO_2, with peaks occurring at around 1300, 450 and 300m in the 2001 data and at 600 m in the 2002 and 2003 data, whereas Tn data (j) is much more irregular. Helium values are flat except for one peak occurring around 650m (k).

Profiles C (Figure 12) and D (Figure 13) were both sampled in 2001 and 2003 for field analysis of CO_2, O_2, Rn and Tn, while CO_2 flux measurements were only conducted in 2001. As above both plots show a correspondence between increased CO_2 (b) and decreased O_2 (c), whereas profile D shows a better correlation between soil gas CO_2 (b) and CO_2 flux (a). Neither Rn (d) or Tn (e) show any clear trends.

Horizontal profile E was only sampled once in 2002 for a limited number of species. The results were essentially featureless for all measured gases and thus these results are not plotted.

Finally horizontal profile F was sampled only once in 2002 for a full suite of gases, however CO_2 flux measurements were not performed. This profile was not one of the original profiles located in 2001, but rather it was added the following year in an effort to examine in more detail the coincident hydrocarbon anomalies observed in the SW of section 7 during the 2001 grid sampling. While this profile did not encounter the extremely high values observed during that season (e.g. 200 ppm C_2H_4), two distinct peaks were observed for the three heavier hydrocarbons which correspond with the location of the previous anomaly (peaks at 200 and 300 m, Figure 14 b, c and d)

3.4. VERTICAL PROFILES

Data from the grid and the horizontal profiles was used to select a limited number of points for vertical profiles in order to define concentration gradients and to determine the minimum depth which is not affected by short-term exchange processes with the atmosphere (e.g. barometric pumping). These profiles were conducted at a total of 6 points over the three years, with samples being collected every 30 cm between 40 and 180 cm depth (depending on local conditions). Only two of these profiles, which were both sampled at two different times, will be discussed here as they are representative of all the vertical profile trends.

Results from sites 13-SW-6 (Figure 15 a) and B23 (Figure 15 b) show the trends of CO_2 during different time periods. In agreement with the data presented thus far, the highest values occurred during the July 2001 campaign while the lowest were found in the fall of 2003. In general the values on both profiles show an increase in concentration with depth, with values increasing rapidly to a depth of 40 or 50 cm below surface followed by a gentle increase below that depth. For example site 13-SW-6 clearly shows this trend, as active exchange with atmospheric air causes dilution of CO_2 in the surface layers while the lack of exchange at depth allows for the progressive production of CO_2 due to the consumption of O_2. This lack of exchange is particularly clear in the two deepest samples from October 2003, which are isolated below a thin clay layer and gave the highest CO_2 values for the entire 2003 campaign. At the same time O_2 values decreased from around 20% to 15% while N_2 values remained constant at 77%, indicating that the CO_2 has not been transported from depth otherwise dilution would have been observed in the nitrogen values. These results indicate two important features in regards to the interpretation of the grid and horizontal profile data. First the chosen sampling depth of 60 to 80 cm is sufficient at the Weyburn site to avoid contamination from atmospheric air. That said it must also be remembered that with the progressively drier seasons the decrease in soil moisture content will result in a general increase in soil air permeability as well as the formation of desiccation cracks which may facilitate deeper exchange with the atmosphere. Second the occurrence of impermeable strata overlying a sampled gas-permeable layer will likely result in anomalously higher CO_2 values compared to a comparable depth at a site having a vertically homogeneous and permeable stratigraphy.

Finally the analysis of various other trace species, including the hydrocarbon gases and helium, did not show any well defined trends.

3.5. ISOTOPES

Three soil gas samples were collected in the summer of 2001 for the analysis of $\delta^{13}C$ in CO_2 in an effort to better understand the origin of the observed anomalies. The samples were all collected in locations with elevated CO_2 concentrations. The isotopic values obtained, along with the concentration values of CO_2 and C_3H_8, are given in Table 2. For comparative purposes the isotopic values of some of the possible sources of the observed soil gas δC^{13} are also given. Obtained values range from –17.3 to –24-6 ‰, values which are well within the range of soil gas CO_2 produced by microbial or root metabolism of organic matter from local plants, and the reasonably large range of values could be due to different plant types or variable dilution with atmospheric air. In addition to the increase in CO_2 concentration with decreasing $\delta^{13}C$, there is also a decrease in the hydrocarbon concentrations over the same interval (e.g. C_3H_8, Table 2) which may indicate that these gases are consumed as CO_2 is produced. Finally the δC^{13} values are substantially higher than that of the injected CO_2, and thus it is believed that these results support the interpretation that the elevated CO_2 values are due to shallow microbiological reactions in the soil.

3.6. CONTINUOUS ^{222}RN PROBE DATA

Not all the probes have operated satisfactorily throughout the full recording periods; the majority have provided continuous data but some have operated for only a few months. However, 3 valuable time series of data have been collected, 2 during winter (2001-2 and 2002-3) and one during summer (2003). Analysis of the data is continuing and will be reported more fully later, but some initial observations are made here.

The atmospheric temperature at the Weyburn field is below freezing for some 4-5 months, whilst the soil temperature at the probe depth usually remains above freezing throughout the year. However, the surface soil does freeze, preventing the escape of soil gases to the atmosphere. This leads to a progressive build up of Rn concentration to near constant levels in mid-winter. The level reached reflects the equilibrium between the input of Rn from depth and loss by alpha decay. This persists for 2 months or more, followed by a relatively rapid decline associated with the spring thaw as gas can once more escape from the soil.

There are other significant seasonal changes in radon concentration. To some extent these reflect changes in atmospheric effects (e.g. pressure and temperature) and are seen at all sites. On the other hand more local effects of soil conditions (e.g. moisture, permeability) are reflected by differences between the probe responses. The observed Rn concentrations for some probes can be modelled to a close approximation as a function of atmospheric pressure and temperature, soil temperature, rainfall and freezing. Rainfall and soil temperature are the main parameters acting on surface ground permeability , which the data show to be an important control on radon concentration in the soils (Figure 16) and on the migration of gas from depth. Where atmospheric pressure has a strong influence on Rn concentration, advective flow of gas is indicated. When diffusion occurs, changes in atmospheric pressure have no effect on the Rn concentration (Pinault and Baubron, 1996). The rate of increase in radon concentration immediately after burial of the probe also provides confirmation of diffusion or advective processes (Fig. 17).

Changes in the Rn concentration that are not linearly correlated to environmental parameters (atmospheric conditions, soil moisture etc.) can be used to examine responses to other effects. Gas velocities, Rn and CO_2 fluxes and permeability can be estimated from the modelling (Pinault and Baubron, 1997).

The results to date indicate gas velocities of up to a maximum of 12 cmh^{-1} where advective gas movement is occurring. CO_2 is a minor component of this gas (about 0.2 %). The relationship between gas velocity and Rn concentration has varied greatly from year to year. As would be expected, calculated soil permeability also shows marked seasonal effects and has varied from year to year; the 2001 and 2002 data are very similar but gas velocities for a given permeability were much lower in 2003. Calculated CO_2 fluxes at 1.9m depth were a tenth to a twentieth of those measured on the surface at 0.013-0.026 $Lm^{-2}h^{-1}$. These probably reflect much lower microbial activity at greater depth within the soil and the lack of plant root respiration, and support the use of indirect CO_2 flux monitoring at depth, whereby masking by biogenic processes is reduced.

3.7. BACKGROUND AREA

As described above, data from a site similar to the Encana phase A1 injection area, yet largely undisturbed by oil exploration and extraction, was needed in order to better interpret the results from the main grid. As much of the data collected thus far appears to indicate that the soil gas concentrations observed over the last three years can be attributed to shallow biological and microbiological respiration pathways, an undisturbed site was needed which had similar soil and crop types, soil moisture contents and topography. The chosen site is located north of Minard's Farm along Highway 35 Table 1 Comparison of three studies which examined the temporal variations of CO_2 concentrations at various depths at a limited number of sites, approximately 10 km to the north west of the main grid (Figure 1 a). Although similar in many ways it should be pointed that the main grid has much more surface water and swampy depressions than the background site. Due to logistical considerations it was not possible to duplicate the main 360 point grid over the background site, but 10% of the number of samples were collected over an area about 2.5% as large.

Gamma spectrometer traverses were carried out at the site to compare soil composition to the main grid and to investigate whether there were any anomalies that might be related to radon and thoron features. This work was undertaken before the soil gas sampling points had been surveyed in, but managed to cover almost two thirds of the soil gas area (Figure 16). There was not enough time to acquire complete coverage. The gamma data show a range of values within that from the main grid area (Figure 17). There are however slight but significant differences revealed by the statistics, which show higher mean (and median) K, U and Th for the background area (Table 3). The two sets of values do show a strong overlap and, bearing in mind that the gamma data from the main grid only cover a fraction of the total area, they are sufficiently similar to suggest that the background site is a reasonable choice, with similar characteristics to the main grid.

Soil gas and gas flux data for the background site are contoured in Figure 18 The distribution of CO_2 in (b) shows higher values in the SE, near the dugout, and in the NW and NE corners. These sites reach maximum values of between 0.9 and 1.3 % and correspond with some of the lowest points on the survey grid (a), implying biological activity in the moister, more organic-rich depressions. When these background data are compared to those from the main grid (Fig. 10a) one can see that the statistical distributions are very similar, with the main difference being the larger number of outliers (i.e. a more skewed distribution) occurring in the latter, up to a maximum value of 2.2%. Although this slight difference could be interpreted as being due to a separate source at the main grid, such as deep CO_2 coming from the injection process, a more likely explanation is that the much larger main grid covers a greater range of soil types, crop types and topography (Table 1) and therefore has the potential to sample a wider range of shallow CO_2-producing environments. This interpretation is supported by other evidence, including the location of CO_2 anomalies in marshy areas adjacent to standing water, the vertical profile results, the relationship of O_2 and N_2 to CO_2 and the isotopic data. He data for the background site also show only atmospheric levels, with no indication of any addition from a deeper source.

The correlation between soil gas CO_2 and CO_2 flux at the background site is quite high, as can clearly been seen by comparing Figures 18b and c. Interestingly, this similarity is much higher for the background site (r^2 = 0.65) than it is when one considers all analysed sites (r^2 = 0.14). As gas flux from the soil to the atmosphere is very closely linked to crop cover, growing cycle, surface moisture conditions and soil type, perhaps this excellent correlation is the result of the relatively small survey area, the brief sampling period (one day) and the limited vegetation covers (wheat stubble, pasture, tilled soil) as compared to the entire 2003 data set as a whole. The statistical distribution of CO_2 flux data from this site is very similar to that of the main grid (Figure 10) except for the fact that there are fewer outliers. As stated above this is probably due to the larger more varied area of the main grid and the greater number of samples collected.

With regard to distribution of the hydrocarbons in soil gas, methane exhibits a unique distribution of generally low concentrations (Figure 18d). In contrast, ethylene, ethane and propane (Figure 18e-g) all show a similar distribution, a weak correlation with elevation and the occurrence of some relatively elevated values. For example, although all hydrocarbon gases from the background site show a similar statistical distribution compared to the main grid (Fig. 10e-h) both ethylene and propane have two of outliers that are higher than those from the main grid, as shown by the classed post symbols in the contour plots. This result may support the interpretation that there are few natural leakage pathways above the CO_2 injection site, as one would expect these heavier hydrocarbons to occur at higher concentrations above a 50 year old oil field having more than 600 deep oil wells which penetrate the entire stratigraphy, than above an essentially non-producing area. That said a contrary hypothesis might be that the depressurisation of the long standing Weyburn oil field has resulted in a decrease in the migration of the hydrocarbon species from the reservoir, and thus the elevated hydrocarbon gases at the background site may be the result of gas leakage from an undiscovered or uneconomic oil reservoir at depth. This interpretation, however, is not supported by the low helium concentrations (all values between 5.24 and 5.25 ppm, not shown) observed at the background site. More research would be required to understand if these gases are due to a shallow or a deep source at this location, but such an effect has been observed, particularly for light hydrocarbons (defined as mainly C_1-C_5 compounds), above other oilfields (e.g. Schumacher and Abrams, 1996; Schumacher and Hitzman, 2001; Schumacher and LeSchack, 2002).

Rn and Tn levels are slightly higher for the background site compared to the grid (Figure 10c-d) as is the case for U and Th series radionuclides measured by gamma spectrometry (Table 3). This suggests slight differences in soil composition between the two areas. Slightly higher Rn values are associated with the areas of higher CO_2, but equally, similar levels are seen where CO_2 concentrations are relatively low (Figure 18h). Tn, on the other hand, appears to have more elevated values in the lower lying areas (Figure 18i) and perhaps a stronger correlation with CO_2 and CO_2 flux distribution.

3.8. DECOMMISSIONED WELLS

One concern with regards to the possible leakage of injected CO_2 to surface is that one or more of the more than 600 oil wells drilled through the overlying stratigraphy into the reservoir may provide a vertical migration pathway should borehole/casing seals be chemically or mechanically compromised. Two very different, inactive well sites were chosen (Figure 1a), in collaboration with Encana personnel, in order to see if any evidence could be found for gases leaking up the well bores from the oil reservoir to surface. The first site, Well 12-18, is completely abandoned; the hole has been cemented shut, the related infrastructure removed and top soil imported to return the site to its original agricultural use. This site, in a grassy field that has been used for pasture for at least the last three years, is located almost in the centre of the main soil gas grid. In contrast, Well 2-25 suffered a casing failure and its operations have been suspended prior to full abandonment. All infrastructure is still in place at this site, including the pump jack, and the gravel access-road/pad is surrounded by a wheat field. Trees bound the southern side of the sampling area, while a small weed-filled depression marks the eastern edge. A total of 16 samples was collected from both sites on a regular 4 x 4 grid with 25 m sample spacing. Contoured data for all the gases analysed from both studied well sites are presented in the various plots of Figure 19.

On the left side of Fig. 19 one can observe that methane, ethane and helium (one point above the atmospheric level of 5.24 ppm) are elevated around the abandoned well (12-18). The two alkanes show a strong spatial correspondence but no relationship with ethylene. This is quite different from the results from the background area, where the heavier hydrocarbon distributions were very similar but the methane distribution was unique. In addition, the statistical distributions for both methane and ethane are elevated with respect to those for the main grid data (Fig. 10 The He anomaly does not correspond with the highest alkane levels. Values for Rn and Tn are generally low.

In contrast, the right side of Fig. 19 shows that CO_2, Rn and Tn are elevated around the suspended well (2-25), while the other gases, particularly the hydrocarbons, are quite low and there are no He anomalies. In addition CO_2, and Rn to a lesser extent, show a statistical distribution which is higher than that seen above the much larger main grid (Fig. 10). Despite this statistical similarity, there is only one point where both these gases have elevated values (immediately SE of the former well head) and there is not a strong similarity between their distributions.

In general it should be noted that none of the gases, at either well site, exhibit elevated concentrations outside the range of values observed above the main grid. Instead, what is observed is that the CO_2 and Rn *populations* at the suspended well and CH_4 and C_2H_6 *populations* at the abandoned well are statistically elevated with respect to that observed for the other sites. Care must be taken in interpreting this type of data due to the bias which may result from the small area sampled and small number of samples collected. No previous soil gas surveys have been conducted in the vicinity of suspended well 2-25, and thus it is not possible to compare the detailed site results with those from the surrounding area. The elevated CO_2 and Rn populations (as opposed to the relatively moderate concentrations) observed above this site are therefore difficult to put into context. That said the lack of corresponding anomalies in the other measured gases, in particular the highly mobile He and CH_4, implies that these values are not due to direct leakage from depth along the failed casing.

Whereas well 2-25 is located to the north of the main grid, well 12-18 is within this grid and thus there exists three years of data for the area surrounding this lease. This area has consistently yielded very low CO_2 values, in agreement with the background to weakly anomalous values observed above the former well head (Fig. 19a). Ethylene also shows very low values in both the detailed and more regional grids, however the values of methane and especially ethane from the detailed grid are anomalously high for the area. This can be illustrated by examining the four main-grid points that surround the detailed grid, each located about 150m from the original well-head location. Methane values are slightly higher for the detailed grid (1 to 3.39 ppm) compared to the four surrounding points (1.4 to 2.1 ppm), whereas ethane values are significantly higher (0.02 to 0.08 ppm as compared to 0.01 to 0.02 ppm, respectively). Again it must be stressed that none of the values observed for the hydrocarbon gases above abandoned well 12-18 are outside the range of values observed for the grid as a whole, only that methane and ethane are elevated with respect to the surrounding area. Present data does not allow for a clear explanation of this difference, however possibilities include remnant hydrocarbon pollution or the site's proximity to an ephemeral stream. Although small scale leakage from the underlying reservoir cannot be totally discounted, the anomalies are small and are more likely due to near surface features, an interpretation supported by the lack of correlation between these gases and helium – only one point gave a slightly anomalous He result (5.29 ppm) and this did not correspond to one of the highest methane values. There are also no matching Rn or Th features (Figure 19).

3.9. RIVER LINEAMENTS

Detailed air-photo and satellite image interpretation of the Weyburn field by J.D. Mollard and Associates (Regina) has outlined a number of lineaments in the area. They are defined by elongated surface water bodies, straight river sections, tonal contrasts and other linear features. While some of these features could be related to shallow processes, such as glacial scouring, lateral lithological variations or even human intervention, it is possible that some may be surface expressions of deep faults, and there is some correspondence between the location and orientation of the lineaments and faulting in the Midale Beds. As a result, these structures could provide a conduit for the migration of gases to the surface, including the injected CO_2. A straight, SW-NE trending section of the seasonal Roughbark Creek was selected for study, and two detailed horizontal soil gas profiles (named G and H) were performed across the water body to monitor for anomalous gas concentrations associated with the lineament (Figure 20). Sample spacing was chosen to maximize detail near the creek while still providing data from 'background' areas further away, thus it varied from 10 m near the creek to 50 m at the ends of the profiles away from the lineament. The profiles predominantly crossed grassy pasture, but some small weed-filled depressions were encountered and brush, bulrushes and other marsh vegetation occurred in the valley (about 3m deep) near to standing water.

Data for the two horizontal profiles (G and H) across the SW-NE river lineament, located just to the north of the main grid, are presented in Figure 20 along with elevation values collected during the surveying of the sampling points. For both profiles there is a clear correlation between topography and CO_2 concentration, with the main river valley (as well as small depressions) having elevated CO_2 and depressed O_2 values. In contrast there appears to be a weak depression of the CH_4 signal where there are peaks of CO_2, particularly along profile G. Rn is also lower where CO_2 is higher whilst Tn is more variable, low for the highest CO_2 on each profile, but relatively high over a weaker CO_2 peak. In general the distribution of the three hydrocarbon species are highly irregular, although there is a weak correlation between CH_4 and C_2H_6 for profile G which is not duplicated in profile H. Instead in profile H there is a clear correspondence between CO_2 and C_2H_4 anomalies located just 2 m beside the river, along with a minimum CH_4 value. He measured in the field does show some anomalous values for Profile G, with a general increasing trend from left to right approaching the creek valley. One of these elevated values coincides with the highest CO_2 value, but the others, all at the south east end of the profile, are associated with very low CO_2 levels. There were no anomalous He values at all on Profile H.

As outlined above these two profiles were conducted to see if the river lineament is a surface expression of a structural discontinuity which could act as a conduit for upwardly migrating gases, in particular for the injected CO_2. If such were the case one would expect to see a pronounced peak of CO_2 in correspondence with the river valley on both profiles, similar to that observed. However, since there are no convincing anomalous values for most of the other gases in correspondence with the lineament (apart from the field laboratory He on Profile G and one C_2H_4 peak on profile H) evidence for such a conduit is very weak. In particular the lack of a clear-cut relationship between CO_2 and He or CH_4, both of which are less reactive and far more mobile than CO_2, indicates that the observed CO_2 peaks are most likely due to near surface biological reactions. This interpretation is supported by the fact that N_2 values, unlike those for O_2, do not show any decrease in correspondence with the CO_2 anomalies; in other words if the CO_2 had a deep origin one would expect to see dilution in both O_2 and N_2. The coincidence of the main CO_2 feature on profile G with an anomalous field laboratory He value, however, does warrant further, more detailed, examination.

3.10. SALT COLLAPSE STRUCTURE

Other possible conduits for upwardly migrating gases may be deep geological features that can be seen in some of the many seismic surveys that have been performed over the Encana oil field. One such feature, highlighted by J.D. Mollard and Associates (Regina), is a salt collapse structure within the Prairie Evaporite. This collapse structure can clearly be observed on seismic sections as a series of vertical offsets that extend slightly, at least at the resolution of the survey, into the overlying unit. The deep structure also appears to be related spatially to lineament zones identified from satellite data. Two horizontal profiles were performed above this structure, with each profile consisting of 10 samples spaced 25 m apart; the profiles crossed each other in the middle forming a NS-EW trending plus sign. The two perpendicular profiles were performed just south of the Encana operations plant and to the east of the main soil gas grid in a very flat, homogenous wheat field (see Figure 1 for location).

The data for the two intersecting horizontal profiles conducted above the salt collapse structure are presented in Figure 21a (N-S) and b (W-E) using the same scales as those used in Figure 20 for the river lineament profiles. It is very clear that this location, which is an extremely homogenous, flat wheat field with no surface water, shows much less concentration variations when compared to the river lineament data. With no depressions to accumulate water and organic matter, the CO_2 concentrations are monotonously flat, lending credence to the belief that the CO_2 peaks on the river lineament profiles are due to shallow biological processes. With regard to the other gases, the only recognizable feature is a CH_4, C_2H_6, He and Rn minimum which corresponds to a C_2H_4 maximum along the N-S profile. There are three small He anomalies in the field laboratory data on the W-E profile but these are not coincident with features in other gases. As such there is no evidence for escape of injected CO_2 or reservoir hydrocarbons along the salt collapse discontinuities, with the levels of gases being comparable or lower than those for the main grid.

4. Discussion

Although the periods of the three field seasons were chosen largely for logistical reasons, the fact that samples were first collected during a hot/wet summer and then during successively cooler and drier fall periods has yielded additional information in terms of possible origins of the observed gas anomalies as well as data on expected minimum and maximum gas concentrations for the region. Based on the statistical analysis of these three data sets given above one can divide the studied gases into four groups: i) those which show a significant concentration decrease, both in the bulk of the samples (median, quartiles) and the outliers, from samples taken in July of 2001 compared to those of September-October 2003 (CO_2, CO_2 flux, C_2H_4 and C_3H_8); ii) those that show an increase over the same period (O_2); iii) those that show a decrease in outliers but the bulk of the samples are relatively constant (CH_4 and C_2H_6); and iv) those that show very little difference in their total statistical distribution (Rn, Tn and N_2). Finally, other gases that were analysed during this project included field and lab analysed helium, as well as the sulphur species CO_2 and SO_2. The field helium analyses are too few to give a statistical interpretation, while lab helium and sulphur gas analyses are of dubious quality and thus will not be discussed here. The cause of the distributions of the various species outlined above, as well as their implications with regard to the study as a whole, are discussed below.

The origin of soil gas CO_2 and CO_2 flux anomalies can be linked to many different sources, the most important being the upward migration of deep gas (which may originate from mantle sources, metamorphic reactions or anthropogenic reservoirs) or shallow biological production. If the source is a deep one, a preferential flow-path would be needed to facilitate this upward migration, such as fault or fracture systems in the overlying sediments. Some of the weakly anomalous to anomalous CO_2 contours appear to be elongated along a NW-SE direction, which is similar to the dominant trends of both the air photo lineaments mapped by J.D.Mollard and Ass. (Regina, Canada) and the fracture patterns observed by Encana personnel in core from the producing horizon. A more detailed comparison, however, only indicates a possible correlation between the soil gas CO_2 distribution and the air photo lineaments in the north-central part of section 12 and along the 1:60000 lineament mapped in the centre of section 13 (compare Figures 1b and 5). In many other areas there is little or no correlation, implying that the CO_2 anomalies may have a more shallow origin.

Instead there is a clear association between the spot CO_2 anomalies and stagnant surface water (sloughs, ephemeral streams and low-lying swampy ground) indicating that perhaps the CO_2 is being produced biologically in moist, organic-rich soils. The process whereby microbial and root respiration produce soil gas CO_2 has been extensively studied (De Jong and Schappert, 1972; Swinnen, 1994; Cheng, 1996), with the relative percentage of these two sources closely linked to the growing season (Rochette et al., 1999). The respiration process can be represented by the simple formula $CH_2O + O_2 \leftrightarrow CO_2 + H_2O$, whereby one mole of oxygen is consumed to produce one mole of CO_2. This type of reaction has been observed in laboratory incubation experiments (Sands et al., 2000) and is clearly observed by graphing O_2 and N_2 against CO_2 for the 2001 Weyburn data (Figure 22 a). A clear inverse relationship exists between O_2 and CO_2 while N_2 vs CO_2 is relatively constant. This graph implies that shallow biological reactions are consuming O_2 and producing CO_2 at a stoichiometric rate of almost 1:1 (slope = -1.1), with CO_2 values trending to a maximum of 20% when O_2 is zero. These data are replicated in all three years, although the error of the slope becomes larger as the concentration of the CO_2 decreases with each successive campaign. In contrast to a biological pathway, if elevated CO_2 values were the result of input from a deeper source one would expect to see dilution of both O_2 and N_2. This type of relationship can be seen for data collected by the Università di Roma 'La Sapienza' at Cava dei Selci in central Italy (Figure 22b), an inhabited area above a quiescent volcanic structure that is known for its degassing of thermogenic CO_2. This graph clearly shows dilution of both O_2 and N_2 as CO_2 concentrations approach 100%, with the slope of the O_2-CO_2 regression line being much less than that for the Weyburn data (-0.19 vs –1.1).

The elevated CO_2 values encountered during the July 2001 sampling campaign can be explained by the hotter and wetter conditions of that period, as both water content and especially soil temperature have been demonstrated to control the rate at which soil CO_2 is produced. Numerous authors have shown that an optimal water content level exists for CO_2 generation, whereby microbial activity is limited by lack of water below the threshold and limited above by reduced gas diffusion rates (Linn and Doran, 1984; Kowalenko et al., 1978; Bouma and Bryla 2000; Risk et al., 2002). This has the effect of causing excessive CO_2 accumulation and lower O_2 in the soil profile (Buyanovsky and Wagner, 1983), as was clearly observed in the vertical profile which penetrated the wet clay horizon (13SW6) as well as throughout the 2001 field season. In fact it has been documented that after a dry soil has been re-wetted the respiration rates can be 370 to 475% higher than before the dry down. (Fierer and Schimel, 2003), a process that is very likely to occur in an area like the Weyburn oilfield which can often undergo drying periods punctuated by intense localised thunderstorms, as encountered during July 2001. With regard to the control of temperature on CO_2 generation, Boone et al. (1998) measured an exponential increase in both root and microbial sources of CO_2 as a function of temperature, while other authors found that temperature was the dominant control on the rate of CO_2 generation in various types of soils (Rochette et al., 1999; Kowalenko et al., 1978; Risk et al., 2002)

A number of studies have been conducted to better understand the seasonal control of environmental parameters on CO_2 generation in the soil horizon, typically consisting of a limited number of vertical profiles being monitored on a weekly to bi-weekly basis. Some of these studies are summarised in Table 4, with maximum concentration values encountered given along with some experimental conditions. In all of these studies minimum CO_2 values were always encountered during the winter while the timing of maximum values depended on the local climate and vegetative cover. Sotomayor and Rice (1999) observed three phases in their data: i) low CO_2 values in winter and spring as limited by temperature; ii) elevated CO_2 during the summer with favourable temperatures and water stimulating microbial and plant growth; and iii) a decrease in CO_2 due to decreased moisture which limited growth and increased the flux potential out of the system. Such temporal trends were observed even to a depth of 1.5 m.

Other researchers have also found increasing CO_2 concentrations with depth (Duenas et al., 1999; Klusman 2003a) despite the fact that the maximal microbial activity can be in the upper layers. Sotomayor and Rice, 1999 attributed this to higher fluxes to the atmosphere in this shallow environment, while another contributing factor can be that the isolation of the deeper sites limits diffusive exchange and promotes the accumulation of CO_2. The results from these studies are in agreement with the increasing trends seen in the vertical profiles performed during the present study, however the significant drop in CO_2 values even at 1 m depths (from 9% in July 2001 to 1% in September-October 2003) indicate that at least some of the Weyburn soils become gas permeable enough during the dry fall to allow for a mass transfer out of the system via flux to the atmosphere.

The link between soil gas CO_2 and CO_2 flux is a complex one, as the two are separated by the mechanics of diffusive transport as controlled by water content variations (Risk et al., 2002) In fact Jensen et al. (1996) found that very large day to day variations in soil surface CO_2 flux can result from rainfall events causing relatively small changes in soil water content, even if CO_2 production rates remained relatively unaffected, while McCarty et al. (1999) discovered experimentally that at air porosities less than 13% there was a marked difference between the CO_2 occurring in the soil pores and the amount of CO_2 transferred to the overlying atmosphere. This storage mechanism may also help explain the local differences observed between the soil gas CO_2 and CO_2 flux distributions at Weyburn, a point supported by the fact that the correlation between these two data sets increases with drier conditions (2001 $r^2 = 0.006$, 2002 $r^2 = 0.056$, 2003 $r^2 = 0.101$). Despite the low correlation it must be reiterated that the general trends of these two measurements are similar, a relationship that was also observed by Sotomayor and Rice (1999) in their study of a cultivated field site.

Like soil gas CO_2, much research has been conducted into environmental and seasonal effects on CO_2 flux rates. For example Sotomayor and Rice, 1999 found that flux rates at a cultivated site ranged from 48 to 193 mg m^{-2} h^{-1}, with the maximum values observed in late July, Klusman (2003a) reported that CO_2 flux values at Rangely, Colorado can vary by an order of magnitude from summer to winter, and De Jong and Schappert (1972) discovered maximum flux rates in June/July and minimum rates in October at a Saskatchewan prairie site. CO_2 flux is also strongly correlated with soil temperature, even at a diurnal level (Tang et al., 2003) although some researchers have found a stronger correlation between flux and soil permeability correlation (Duenas et al., 1999)

The theory that the observed CO_2 at the Weyburn site is of biogenic origin is further supported by the carbon isotopic analyses conducted on CO_2 in three samples collected in 2001. Numerous studies in the literature have shown that the isotopic signature of respired soil gas CO_2 is essentially the same as plants typically sown at that site (Schonwitz et al., 1986; Cheng, 1996). Complicating the situation, however, is that if crops of different signatures (i.e. C1 vs C2 type plants) are rotated on the same land the isotopic signature of the soil carbon will not be as well defined. In any case the range of values observed for the collected samples fall well within the range expected for the locally grown vegetation, and variations can be explained by different levels of exchange with atmospheric air and a carbon source having a heterogeneous isotopic signature.

Finally there is generally is no correlation between CO_2 anomalies and CO_2 injection wells (marked by stars in Figure 1b), and there is also no obvious link between the anomalies and the buried CO_2 pipelines (not shown).

In terms of other gases, the plot of Rn concentration relative to CO_2 (Figure 23) generally shows a poor correlation between the two gases. The large scatter is consistent with a mainly diffusion-driven gas flow at most of the sites analysed, as a more direct relationship between CO_2 and Rn would indicate advective processes, with CO_2 acting as a carrier for Rn (Kristiansson and Malmqvist, 1982; Varhegyi et al., 1986; Etiope and Lombardi, 1996).

As described above the hydrocarbon species show two different trends when the three data sets are compared statistically. Whereas ethylene and propane show a trend which is very similar to that of CO_2 and CO_2 flux, in that both outliers and the bulk of samples decrease from the first to the last sampling campaigns (Figure 4), methane and ethane have outliers that decrease but the bulk of the samples have a relatively consistent range of values.

The behaviour of methane is relatively straightforward, aside from a few outliers above 3 ppm, as the observed values are fairly typical for aerobic soils like those found at Weyburn. CH_4 is generally consumed in aerobic soils by methanotrophic bacteria, with the source of this consumed gas being from greater depths or from the atmosphere. In fact CH_4 fluxes to the atmosphere can be negative as atmospheric methane is drawn into the soil and consumed, which would be indicated by a decreasing concentration with depth (Klusman, 2003b, Duenas et al., 1999). Such a result was generally found for the Weyburn vertical profiles, which is in sharp contrast with the highly increasing trends observed in some of the deep profiles conducted by Klusman (2003a) at the Rangely EOR site in Colorado. The relatively low solubility, high mobility and low reactivity of methane (Jones and Drozd, 1983; Philp and Crisp, 1982) means that if there is a preferential vertical pathway it should migrate much more quickly than CO_2 and arrive in the near surface environment at elevated concentrations. Instead the very slight increase observed in the median and outlier values with each successive sampling may rather be a indication that cooler temperatures and drier soils decrease the activity of the methanotrophs and increase soil gas permeability, resulting in the bulk of samples increasing slightly from around 1ppm towards the atmospheric concentration of around 2.5ppm. The few outlier samples that exceed 3 ppm (5 in 2001, 4 in 2002 and 3 in 2003) are more difficult to explain, as the only other sources of methane would be anaerobic microbiologically produced (but no sample was anoxic), deep sourced (but this is not supported by the other gases like Rn and CO_2) or due to leaking infrastructure (but elevated sites were not always reproduced year-on-year).

The distribution of the heavier hydrocarbons are even more pronounced, with particularly anomalous values being encountered during the first sampling campaign of July 2001. These values are extremely anomalous based on the experience of the authors, particularly the values of ethylene on the order of 100 – 200 ppm. Of the heavier hydrocarbons only ethylene is believed to be a product of biological reactions, as experiments have shown a correlation between CH_4 and minor amounts of C_2H_4 in the anaerobic fermentation of organic matter (Jones et al., 2000). In contrast the heavier hydrocarbons are typically thought to result only from the thermo-catalytic reactions associated with petrogenic deposits, and thus a C1/C2 ratio less than 500, or a C1/(C2+C3) less than 1000, are often interpreted as being representative of a deep origin. The latter ratio was calculated for the 2003 data for both the grid and the background site, and the resulting values are very low for both sites (grid median = 19, background median = 16); similar data was found for the other two years. Although the high values of the heavier hydrocarbons and the low C1/(C2+C3) ratios are difficult to reconcile with other results, the fact that both the oil field and background site ratio values are very similar may indicate that the observed values are not due to leakage from the reservoir.

Possible explanations for these values and the variations between sampling periods include seasonal effects, temporally variable gas releases from natural or man-made sources, and sample contamination. In regards to the first, biological reactions appear unlikely based on the reasoning outlined above. Temporal variability of the input function is more likely, however it is difficult to define the source and the reason for the change. In theory gas flux from depth along fractures can be influenced by such natural events as earth tides or changes in pressure relationships at depth, however the fact that other gases did not show similar outliers in the 2001 survey does not support this hypothesis. An intermittent leak from a man-made structure like a buried pipeline is also theoretically possible, however the nearest pipeline is located 40m to the east of this point and thus not a very likely source. Finally the possibility of sample contamination can not be ignored, however this possibility is not supported by the fact that values of this magnitude have not been seen by the authors over the last 15 years of using this method, and the fact that the elevated samples are spatially dispersed and were sampled on different days. Further research at the sites of the original anomalies, preferably during the summer months to duplicate the original conditions, would be required to better understand these results.

5. Summary and Conclusions

Application of soil gas and gas flux measurements to study EOR and/or CO_2 sequestration sites is extremely rare, with the only ones known to the authors being the works of Klusman (2003 a, b) on the Rangely site in Colorado (USA). This site, however, has significant differences compared to Weyburn, particularly the fact that CO_2 injection has taken place over the last 19 years as compared to the 3.5 years at Weyburn. The principle conclusion of Klusman (2003a) is that a small (relative to the stored amount) but measurable quantity of injected CO_2 is leaking to the surface at the Rangely EOR site. In contrast there is very little evidence that microseepage of injected CO_2 has occurred to date at Weyburn, either because the cap rock at this site is less permeable or because sampling began shortly after the start of CO_2 injection. In this sense one of the main goals of the Weyburn soil gas work has been achieved, as a large background database now exists for the site to which future results can be compared.

As outlined previously the principal goals of the present research project were to monitor gases within the shallow horizon in order to establish natural background concentrations and to ascertain if there is a leak of CO_2, or associated tracer gases, as a direct result of the solvent flood presently occurring at the Encana Weyburn oil field. At the completion of the three year project a large amount of data has been collected which addresses these questions.

Sampling of the large 360 point grid above the injection area over the last three years showed CO_2, O_2 and CO_2 flux values in the range of natural soils, and these observed levels can be explained by standard metabolic pathways that normally occur in the shallow soil horizon. The spatial anomaly distributions of these gases are reasonably reproducible from year to year and season to season, despite the fact that the range of values vary from high concentrations in the hot wet summer of 2001 to the low values found in the fall of 2002 and 2003. In contrast to these biologically active species, the statistical and spatial distribution of radon and thoron is very similar from one sampling season to the next. This provides support for the idea that leakage is not taking place, as one would expect to see high radon during the periods of high CO_2 if the latter was acting as carrier for the more trace former gas. Hydrocarbon values were found to be within normal ranges in the autumn of 2003, however the previous two seasons showed elevated values which were not fully expected. In fact ethylene and propane show a statistical distribution over the three years which is quite similar to that of CO_2, whereas methane and ethane have relatively constant values except for more concentrated outliers during the first and second seasons. As the heavier hydrocarbons do not normally originate via shallow biological reactions it is difficult to reconcile these results with those of the other gases.

A comparison of the grid data with that of the background site, located in similar surface geology but outside the Weyburn oil field, shows a very similar statistical distribution for all monitored parameters. This result supports the interpretation that the observed gas concentrations are not due to deep leakage. In particular both sites have a very similar $CH_4/(C_2H_6 + C_3H_8)$ ratio. This value is low and in the range of thermo-catalytic regime, however the fact that such a value was found both within and outside the oil field implies that the origin of these gases are not necessarily from a deep oil reservoir.

Highly detailed horizontal profiles performed across radon and CO_2 anomalies defined during the first year sampling of the main grid were used both to select sites for the installation of the long term radon monitoring probes, as well as to study in detail the elevated soil gas concentrations and to relate them to surface lineaments. The work conducted on these profiles showed reproducible trends for CO_2, CO_2 flux and, to a lesser extent, radon, with anomalies occurring in correspondence with low lying areas and surface water. Although some of these coincide with mapped lineaments which could in theory be the surface expression of deep faults, it is perhaps more likely that these lineaments are shallow features that accumulate water and nutrients and thus produce biologically created anomalies.

Work was also performed on a number of sites which could represent possible vertical migration pathways, including two decommissioned wells, a river lineament and a salt collapse structure with its associated faulting. Sampling over these areas showed very little in the way of clear indications of deep gas leakage. Data from the salt collapse structure was extremely low. Results from the river lineament gave a clear CO_2 anomaly in the valley and an increasing He trend in the area of the river; the former was interpreted as being of a shallow origin while the latter is presently not fully understood. The values obtained around the former oil wells were within the range of values observed over the main grid, although the CO_2 median from one site was slightly higher.

Continuous Rn monitoring data has been collected over two winters (2001-2 and 2002-3) and one summer (2003). The results provide a more detailed picture of seasonal changes in soil gas concentration. The data indicate diffusive and advective gas flow at different sites, with maximum derived gas velocities of $12cmh^{-1}$. Rainfall and soil temperature have a controlling effect on surface soil permeability and therefore on Rn concentrations in the soil gas. CO_2 is estimated to make up a very small proportion of the gas at depth in the soil (around 0.2%) and calculated CO_2 fluxes are only 5-10% of those at the surface due to reduced microbial activity and plant root respiration.

6. References

BOONE R.D., NADELHOFFER K.J., CANARY J.D. and KAYE J.P. 1998. Roots exert a strong influence on the temperature sensitivity of soil respiration. *Nature*, Vol. 396, 570-572.

BOUMA T.J. and BRYLA D.R. 2000. On the assessment of root respiration for soils of different textures: interactions with soil moisture contents and soil CO_2 concentrations. *Plant and Soil*, Vol. 227, 215-221.

BUYANOVSKY G.A. and WAGNER G.H. 1983. Annual cycles of carbon dioxide level in soil air. *Soil Science Society of America Journal*, Vol. 47, 1139-1145.

CHENG W. 1996. Measurement of rhizosphere respiration and organic matter decomposition using natural ^{13}C. *Plant and Soil*, Vol. 183, 263-268.

CHIODINI, G., FRONDINI, F.and PONZIANI, F. 1995. Deep structures and carbon dioxide degassing in central Italy. *Geothermics*, Vol. 24, 81-94.

CHIODINI, G., CIONI, R., GUIDI, M., MARINI, L. and RACO, B. 1998. Soil CO_2 flux measurements in volcanic and geothermal areas. *Applied Geochemistry*, Vol. 13, 543-552.

CHIODINI, G., FONDINI, F., KERRICK, D.M., ROGIE, J., PARELLO, F., PERUZZI, L. and ZANZARI, A.R. 1999. Quantification of deep CO_2 fluxes from Central Italy. Examples of carbon balance for regional aquifers and soil diffuse degassing. *Chemical Geology*, Vol. 159, 205-222.

CHIODINI G. and FRONDINI F. 2001. Carbon dioxide degassing from the Albani Hills volcanic region, Central Italy. *Chemical Geology*, Vol. 177, 67-83.

CIOTOLI G., ETIOPE G., GUERRA M. and LOMBARDI S. 1999. The detection of concealed faults in the Ofanto Basin using the correlation between soil-gas fracture surveys. *Tectonophysics*, Vol. 301, 321-332.

CIOTOLI G., GUERRA M., LOMBARDI S. and VITTORI E. 1998. Soil gas survey for tracing seismogenic faults: a case-study in the Fucino basin (central Italy). *Journal of Geophysical Research*, Vol. 103 B(10), 23,781-794.

DE JONG E. and SCHAPPERT H.J.V. 1972. Calculation of soil respiration and activity from CO_2 profiles in the soil. *Soil Science*. Vol. 113, 328-333.

DUENAS C., FERNANDEZ M.C., CARRETERO J. and LIGER E. 1999. Methane and carbon dioxide fluxes in soils evaluated by ^{222}Rn flux and soil air concentration profiles. *Atmospheric Environment*, Vol. 33, 4495-4502.

ETIOPE, G. and LOMBARDI, S. 1996. Laboratory simulation of geogas flow. *Environmental Geology*, Vol. 27, 226-232.

FIERER N. and SCHIMEL J.P. 2003. A proposed mechanism for the pulse in carbon dioxide production commonly observed following the rapid rewetting of a dry soil. *Soil Science Society of America Journal*, Vol. 67, 798-805.

HINKLE, M. 1994. Environmental conditions affecting concentrations of He, CO_2, O_2 and N_2 in soil gases, *Applied Geochemistry* Vol. 9, 53-63.

JENSEN L.S., MUELLER T., TATE K.RL., ROSS D.J., MAGID J. and NIELSEN N.E. 1996. Soil surface CO_2 flux as an index of soil respiration in situ: a comparison of two chamber methods. *Soil Biology and Biochemistry*, Vol. 28, 1297-1306.

JONES V.T. and DROZD R.J. 1983. Prediction of oil or gas potential by near-surface geochemistry. *Bulletin of the American Association of Petroleum Geologists*, Vol. **67**, 932-952.

JONES V.T., MATTHEWS M.D. and RICHERS D.M. 2000. Light hydrocarbons for petroleum and gas prospecting. In: *Handbook of Exploration Geochemistry. Volume 7. Geochemical Remote Sensing of the Sub-Surface*. M. Hale (editor) (Amsterdam: Elsevier).

KLUSMAN R.W. 2003a. Rate measurements and detection of gas microseepage to the atmosphere from an enhanced oil recovery/sequestration project. Rangely, Colorado, USA. *Applied Chemistry*, Vol. 18, 1825-1838.

KLUSMAN R.W. 2003b. Computer modelling of methanotrophic oxidation of hydrocarbons in the unsaturated zone from an enhanced oil recovery/sequestration project. Rangely, Colorado, USA. *Applied Chemistry*, Vol. 18, 1839-1852.

KLUSMAN R.W. 1993. *Soil gas and related methods for natural resource exploration.* (Chichester: J. Wiley & Sons).

KOWALENKO C.G., IVARSON K.C. and CAMERON D.R. 1978. Effect of moisture content, temperature and nitrogen fertilization on carbon dioxide evolution from field soils. *Soil Biology and Biochemistry*, Vol. 10, 417-423.

KRISTIANSSON, K. and MALMQVIST, L. 1982. Evidence for non diffusive transport of ^{222}Rn in the ground and a new physical model for the transport. *Geophysics*, Vol. 47, 1444-1452.

LINN D.M. and DORAN J.W. 1984. Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and non tilled soils. *Soil Science Society of America Journal*, Vol. 48, 1267-1272.

LOMBARDI S. , BENVEGNÙ F., BRONDI A. and POLIZZANO C. 1993. Field investigation with regard to the impermeability of clay formations: Helium-4 soil gas surveys in sedimentary basins as a tentative study of secondary permeability in clayey sequences - *Commission of the European Communities, Nuclear Science and Technology. Report EUR 14585 EN.*

LOMBARDI S., ETIOPE G.,GUERRA M., CIOTOLI G., GRAINGER P., DUDDRIDGE G.A., GERA F., CHIANTORE V., PENSIERI R., GRINDROD P. and IMPEY M. 1996. The refinement of soil gas analysis as a geological investigative technique. *Commission of the European Communities, Nuclear Science and Technology. Final report. EUR 16929 EN*

MCCARTY G.W., SHELTON D.R. and SADEGHI A.M. 1999. Influence of air porosity on distribution of gases in soil under assay for denitrification. *Biology and Fertility of Soils*, Vol. 30, 173-178.

PHILP R.P and CRISP P.T. 1982. Surface geochemical methods used for oil and gas prospecting - A review. *Journal of Geochemical Exploration*, Vol. **17**, 1-34.

PINAULT J-L. and BAUBRON J-C. 1996. Signal processing of soil gas radon, atmospheric pressure, moisture, and soil temperature data : a new approach for radon concentration modelling. *Journal of Geophysical Research,* Vol. 101, 3157-3171.

PINAULT J-L. and BAUBRON J-C. 1997. Signal processing of diurnal and semidiurnal variations in radon and atmospheric pressure: a new tool for accurate in situ measurement of soil gas velocity, pressure gradient, and tortuosity. *Journal of Geophysical Research,* Vol. 102, 18101-18120.

RISK D., KELLMAN L., and BELTRAMI H. 2002. Soil CO_2 production and surface flux at four climate observatories in eastern Canada. *Global Biogeochemical Cycles*, Vol. 16, 69-80.

ROCHETTE P., FLANAGAN L.B. and GREGORICH E.G. 1999. Separating soil respiration into plant and soil components using analyses of the natural abundance of carbon-13. *Soil Science Society of America Journal.* Vol. 63, 1207-1213.

SANDS R., NUGROHO P.B., LEUNG D.W.M., SUN O.J. and CLINTON P.W. 2000. Changes in soil CO_2 and O_2 concentrations when radiata pine is grown in competition with pasture or weeds and possible feedbacks with radiata pine root growth and respiration. *Plant and Soil*, Vol. 225, 213-225.

SCHONWITZ R., STICHLER W. and ZIEGLER H. 1986. $\delta^{13}C$ values of CO2 from soil respiration on sites with crops of C3 and C4 type of photosynthesis. *Oecologia*, Vol. 69, 305-308.

SCHUMACHER, D and ABRAMS, M. A. (editors) 1996. Hydrocarbon Migration and Its near-Surface Expression. *American Association of Petroleum Geologists Memoir,* No. 66.

SCHUMACHER, D and HITZMAN, D. C. 2001. Geochemical exploration in mature basins: new applications for field development and production. Extended abstract No. 011, 1-8. In: *Rock the foundation convention, June 18-22, 2001*, (Calgary: Canadian Society of Petroleum Geologists).

SCHUMACHER, D. and L A. LESCHACK (editors) 2002. Surface Exploration Case Histories: Applications of Geochemical, Magnetic, and Remote Sensing. *American Association of Petroleum Geologists Studies in Geology*, No. 48, *SEG Geophysical References Series*, No. 11

SINCLAIR A.J. 1991. A fundamental approach to threshold estimation in exploration geochemistry: probability plots revisited. *Journal of Geochemical Exploration,* Vol.41, 1-22.

SOTOMAYOR D. and RICE C.W. 1999. Soil air carbon dioxide and nitrous oxide concentrations in profiles under tallgrass prairie and cultivation. *Journal of Environmental Quality*, Vol. 28. 784-793.

SWINNEN, J. 1994. Evaluation of the use of a model rhizodeposition technique to separate root and microbial respiration in soil. *Plant and Soil*, Vol. 165, 89-101.

TANG J. BALDOCCHI D.D., QI Y. and XU L. 2003. Assessing soil CO_2 efflux using continuous measurements of CO_2 profiles in soils with small solid state sensors. *Agricultural and Forest Meteorology*, Vol. 118, 207-220.

TEDESCO, S. A. 1995. *Surface geochemistry in petroleum exploration*. (New York: Chapman and Hall).

VARHEGYI, A., BARANYI, I. and SOMOGYI, G. 1986. A model for the vertical subsurface radon transport in “geogas” microbubbles. *Geophysical Transaction*, Vol. 32, 235-253.

Table 1 Summary of the sites examined during this study. Note that weeds are listed in the column 'dominant vegetation' because these were often associated with surface water, organic rich soil and elevated CO_2 values.

	Number of samples	Sample spacing (m)	Sample area (km^2)	Sample density (s/km^2)	Dominant vegetation	Topography
Main grid	360	200	14.4	25	wheat, weeds, tilled soil, flax, pasture,	much surface water, depressions, undulating ground
Background grid	37	100	0.35	100	wheat, weeds, tilled soil	undulating ground
Horizontal profile A	59	25	-	-	wheat, tilled soil, weeds	undulating ground, some surface water
Horizontal profile B	61	25	-	-	wheat, oil seed, weeds	undulating ground, much surface water
Horizontal profile C	45	25	-	-	Wheat, weeds	undulating ground, parallels creek with depressions at S end
Horizontal profile D	45	25	-	-	wheat	flat
Horizontal profile E	36	25	-	-	wheat, weeds in valley	undulating plus creek valley
Horizontal profile F	45	25	-	-	wheat	undulating ground
Well 12-18 (no infrastructure)	16	25	0.01	1600	pasture	flat
Well 2-25 (infrastructure)	16	25	0.01	1600	wheat, weeds, trees	flat with weedy depression
River lineament horizontal profile G	36	10-50	-	-	pasture, weeds, bulrushes	undulating plus creek valley
River lineament horizontal profile H	29	10-50	-	-	pasture, weeds, bulrushes	undulating plus creek valley
Salt collapse structure	20	25	-	-	wheat	very flat

Table 2 Measured isotopic values from 3 soil gas samples collected in 2001 and analysed by the University of Calgary, along with the concentration of CO_2 and C_3H_8 in each sample. Typical values of possible sources of this CO_2 are also given for comparative purposes.

Samples	**δC^{13} CO_2**	**CO_2 (%)**	**C_3H_8 (ppm)**
Weyburn 19SE-5	-17.3	4.1	1.62
Weyburn 13SE-13	-21	4.4	0.83
Weyburn 13SW-6	-24.6	8.1	0.48
Comparative values			
C3 plants (e.g. wheat)	-35 to –21 ‰		
C4 plants (e.g. corn)	-21 to –9 ‰		
Injected CO_2	-35		
Atmospheric CO_2	-11		

Table 3. Summary of main statistical parameters for gamma spectrometry results at the main soil gas grid and background site in 2003

	Site	Valid Number	Mean	Median	Min.	Max.	Lower Quartile	Upper Quartile	Std.Dev.	Percent Std.Dev.
Total gamma	main grid	7515	44.6	44.0	29.6	63.9	41.0	47.3	5.4	12.0
cps	background	1838	48.2	48.7	24.4	55.1	47.3	50.1	3.9	8.2
K	main grid	7515	1.3	1.3	0.6	1.9	1.2	1.4	0.2	11.6
%	background	1838	1.4	1.4	1.0	1.8	1.3	1.5	0.1	10.0
U	main grid	7515	2.2	2.0	-0.2	7.6	1.5	2.8	1.1	50.7
ppm	background	1838	2.5	2.4	0.4	5.0	2.0	2.9	0.7	29.1
Th	main grid	7515	5.4	5.3	1.7	10.4	4.6	6.3	1.2	22.9
ppm	background	1838	6.3	6.3	2.8	10.4	5.6	7.1	1.1	17.3

Table 4 Comparison of three studies which examined the temporal variations of CO_2 concentrations at various depths at a limited number of sites

Reference	Vegetation type	Maximum depth studied	Maximum CO2 concentration	sites studied	Sampling regime
Buyanovsky and Wagner, 1983	wheat	50 cm	8 %	3	Sampled vertical profiles every 2-3 weeks for 24 months
Sotomayor D. and Rice C.W., 1999	Prairie grasses and wheat	150 cm	6.4 % grass 3.6 % wheat	6	Sampled vertical profiles every 2 weeks for 17 months
Risk et al., 2002	Forest and field	100 cm	0.3 %	4	Sampled vertical profiles weekly for 2 years

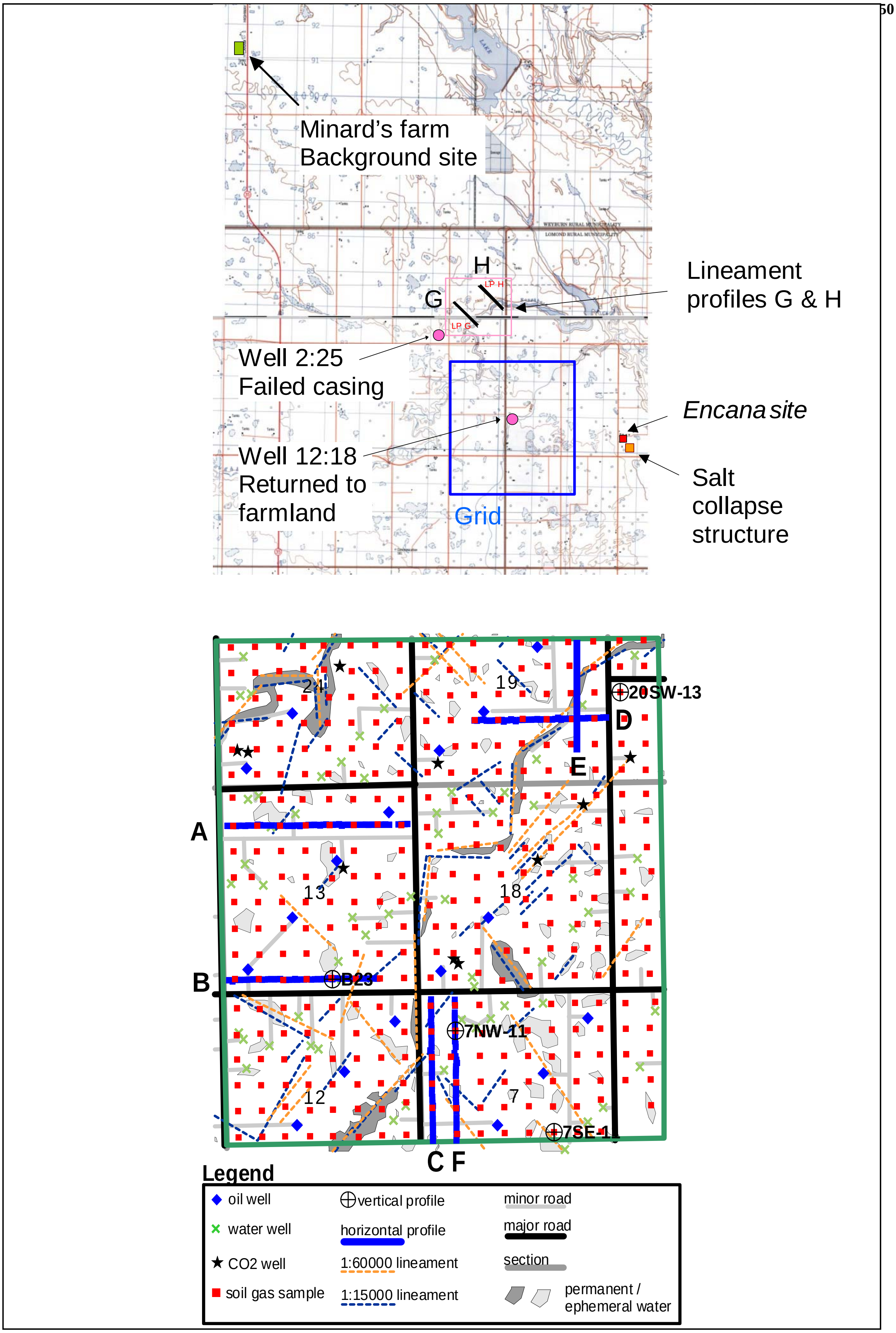


Figure 1 Maps showing the locations of the various studied sites (a) as well as a detail of the grid area (b) showing sampling points, surface water, wells and air photo lineaments. Note that the air photo lineaments were kindly provided by J.D. Mollard and Associates of Regina (Canada).

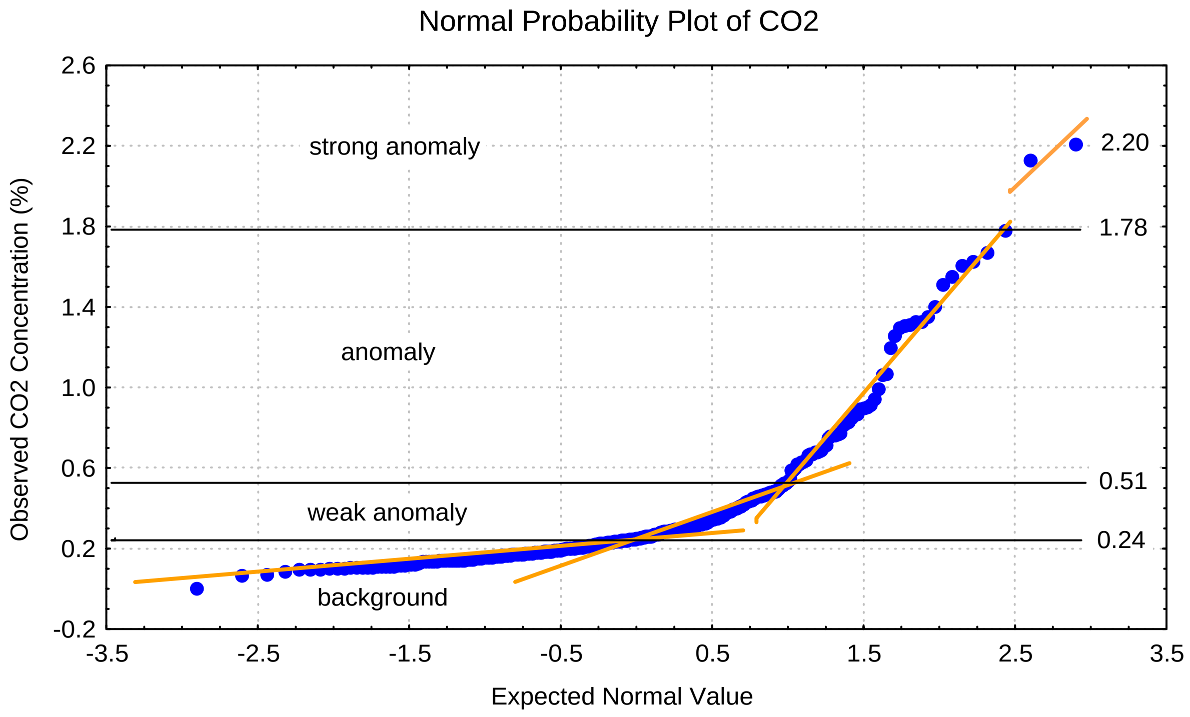


Figure 2 Normal probability plot showing the method used for defining data set populations for each parameter, with CO_2 values obtained over the main grid as an example. Note that the boundaries defined for the main grid have been used for the plotting of all studied sites in order to facilitate comparisons and to put the various values in a more regional context.

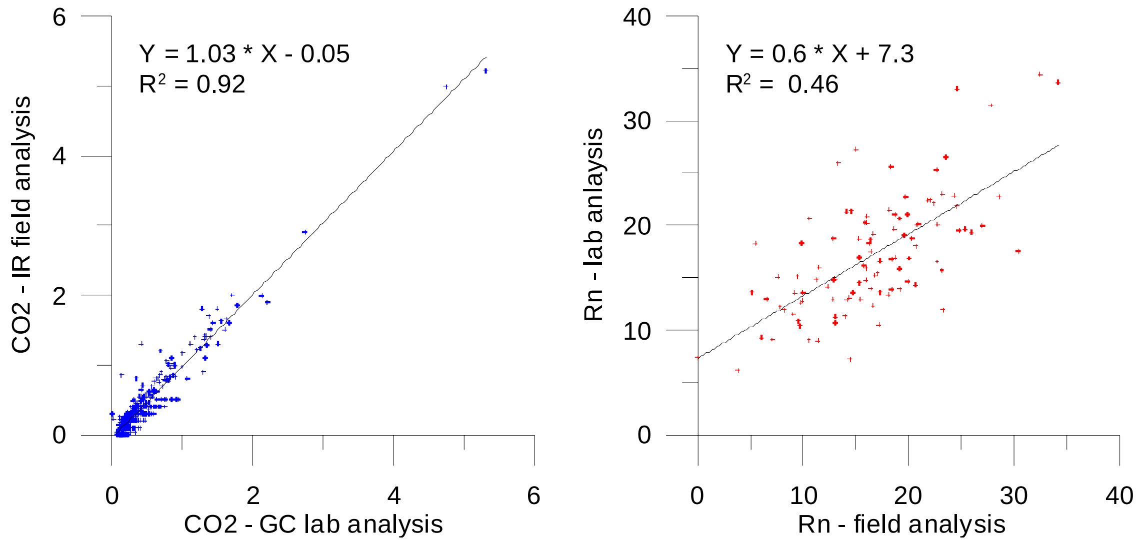


Figure 3 Graphs comparing the results from different analytical techniques used during the present research. Graph (a) shows an excellent correlation between field infrared and lab gas chromatograph analyses for CO_2, with an almost perfect slope of unity. A comparison of the two methods used for radon (b) do not give such a similar correlation due to the more difficult nature of this measurement.

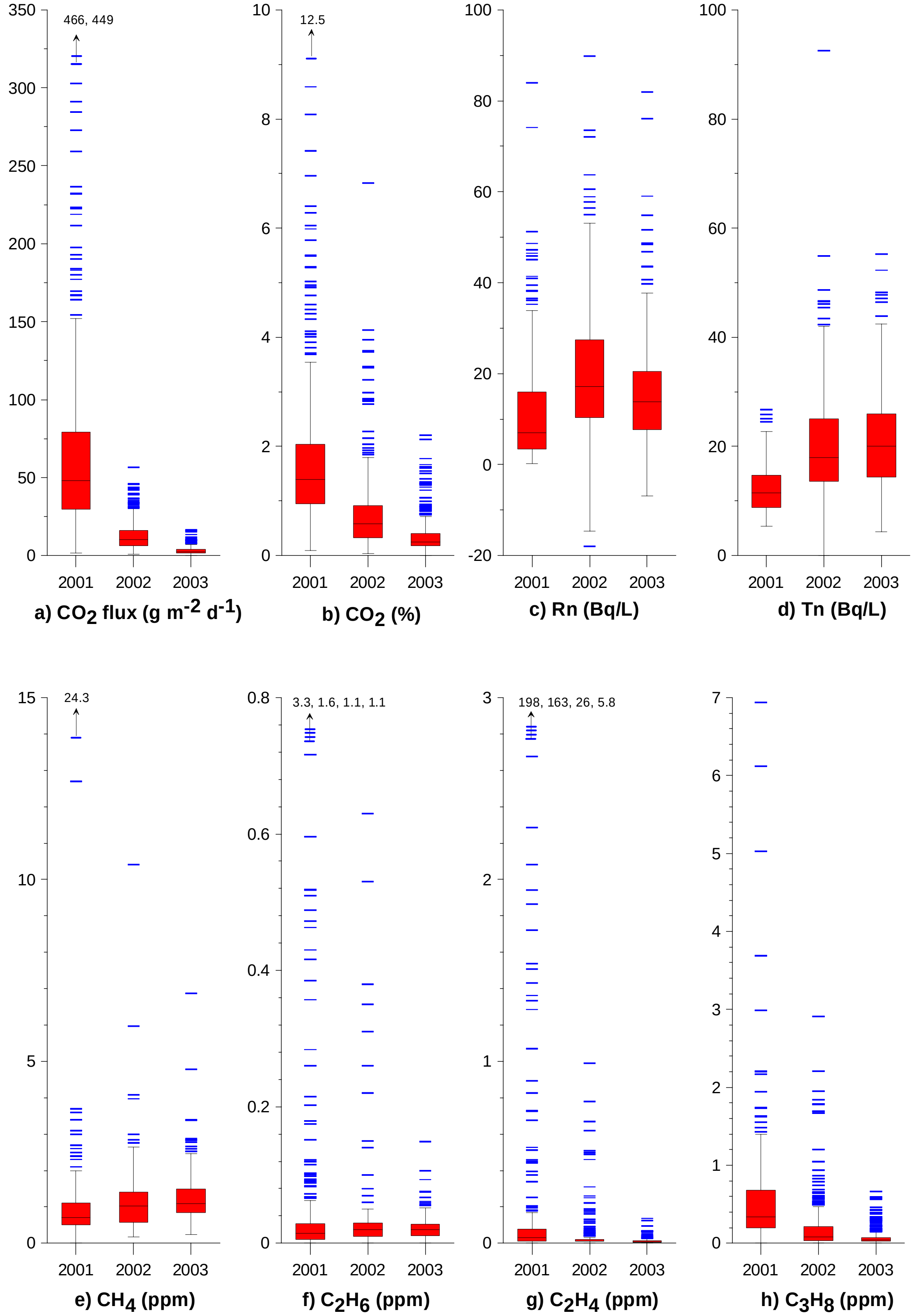


Figure 4 Box and whisker plots for gas flux and some of the soil gases measured on the main grid for each of the three years of the project. CO_2 flux, CO_2, ethylene and propane all decrease substantially with each successive field campaign, whereas radon and thoron are relatively constant and methane and ethane decrease primarily only in the outlier values. Note that off-scale values are represented with an arrow and the respective numerical value(s).

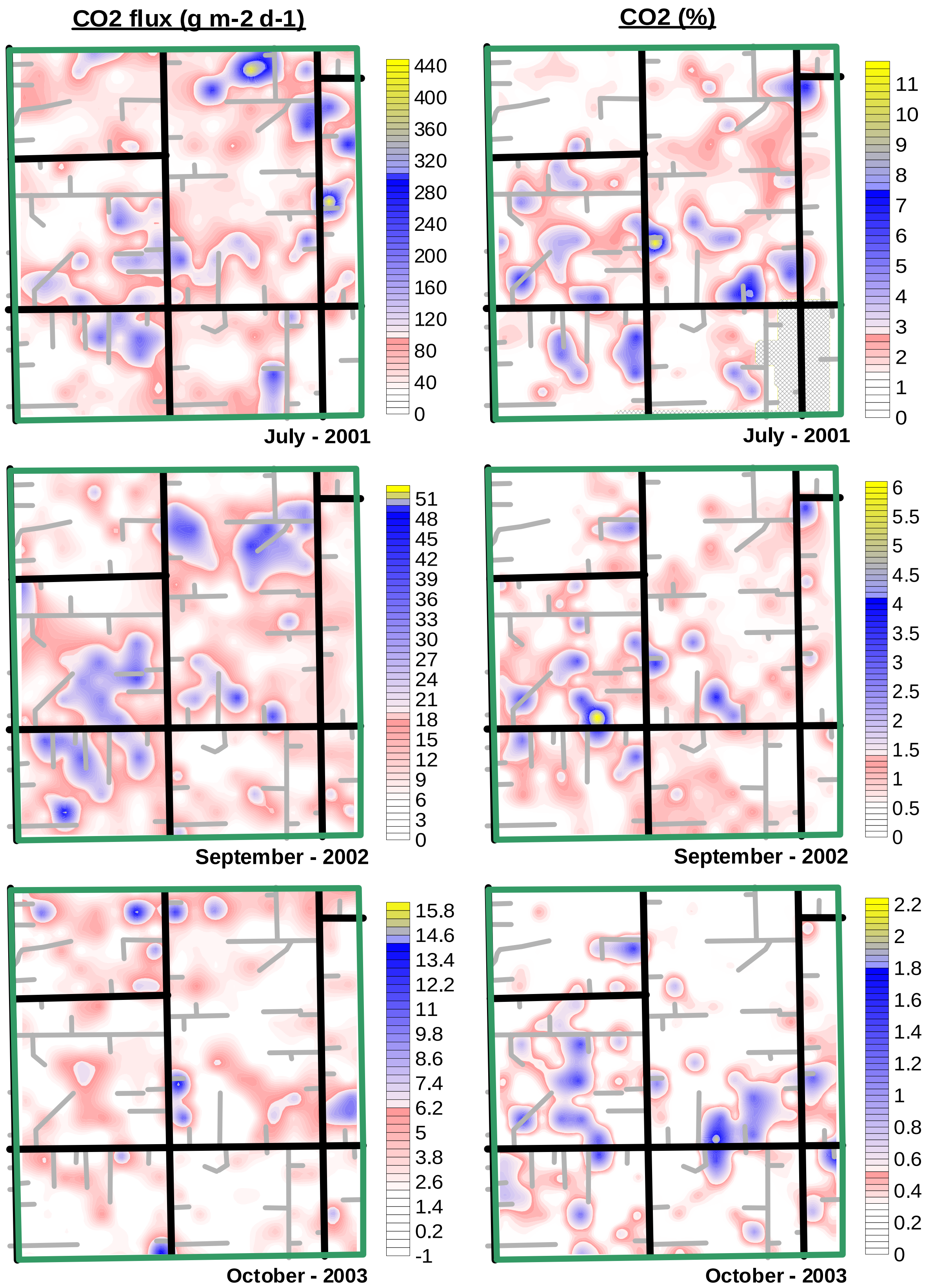


Figure 5 Contoured distribution of CO_2 flux and soil gas CO_2 for the three sampling campaigns

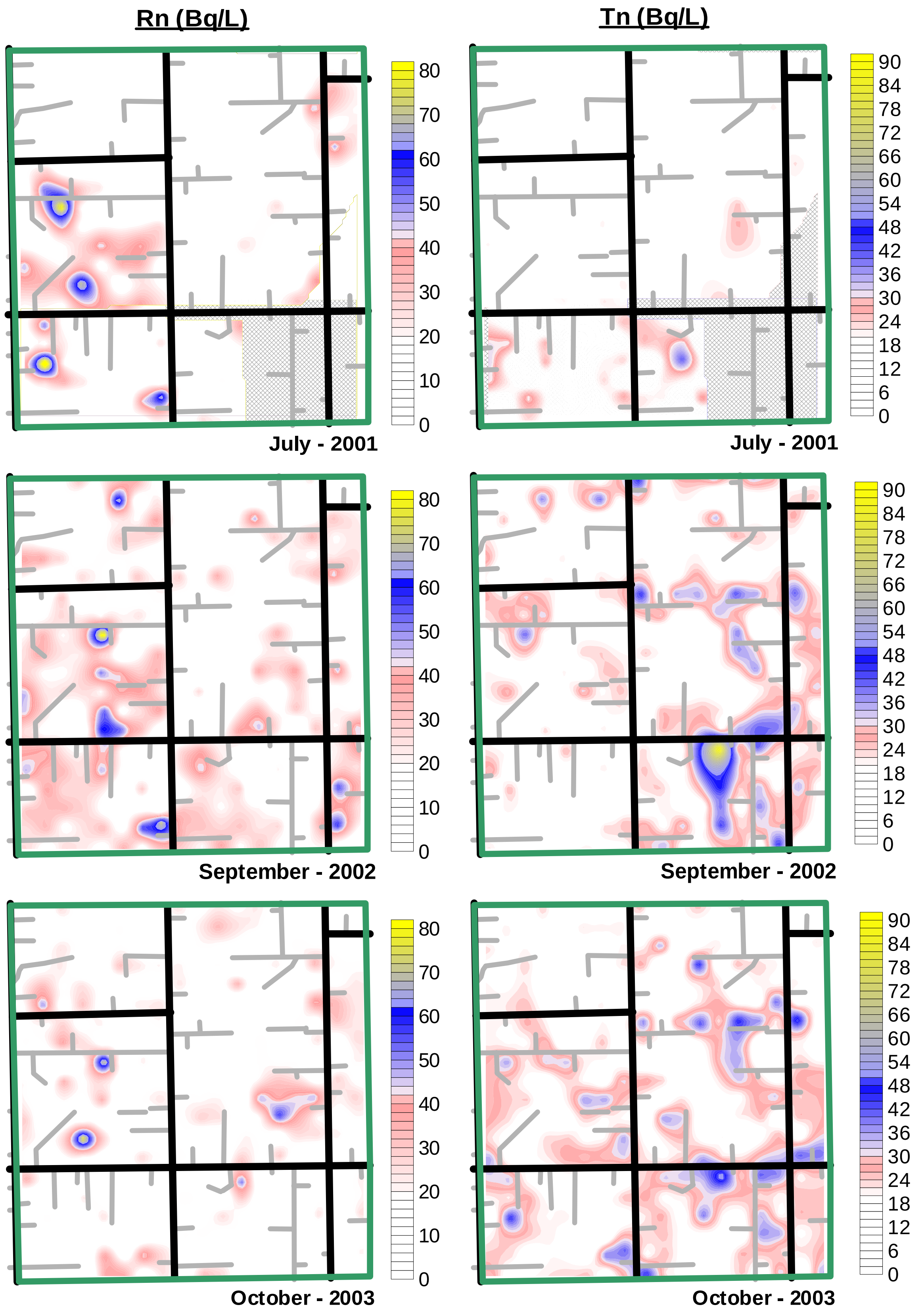


Figure 6 Contoured distribution of soil gas radon and thoron for the three sampling campaigns

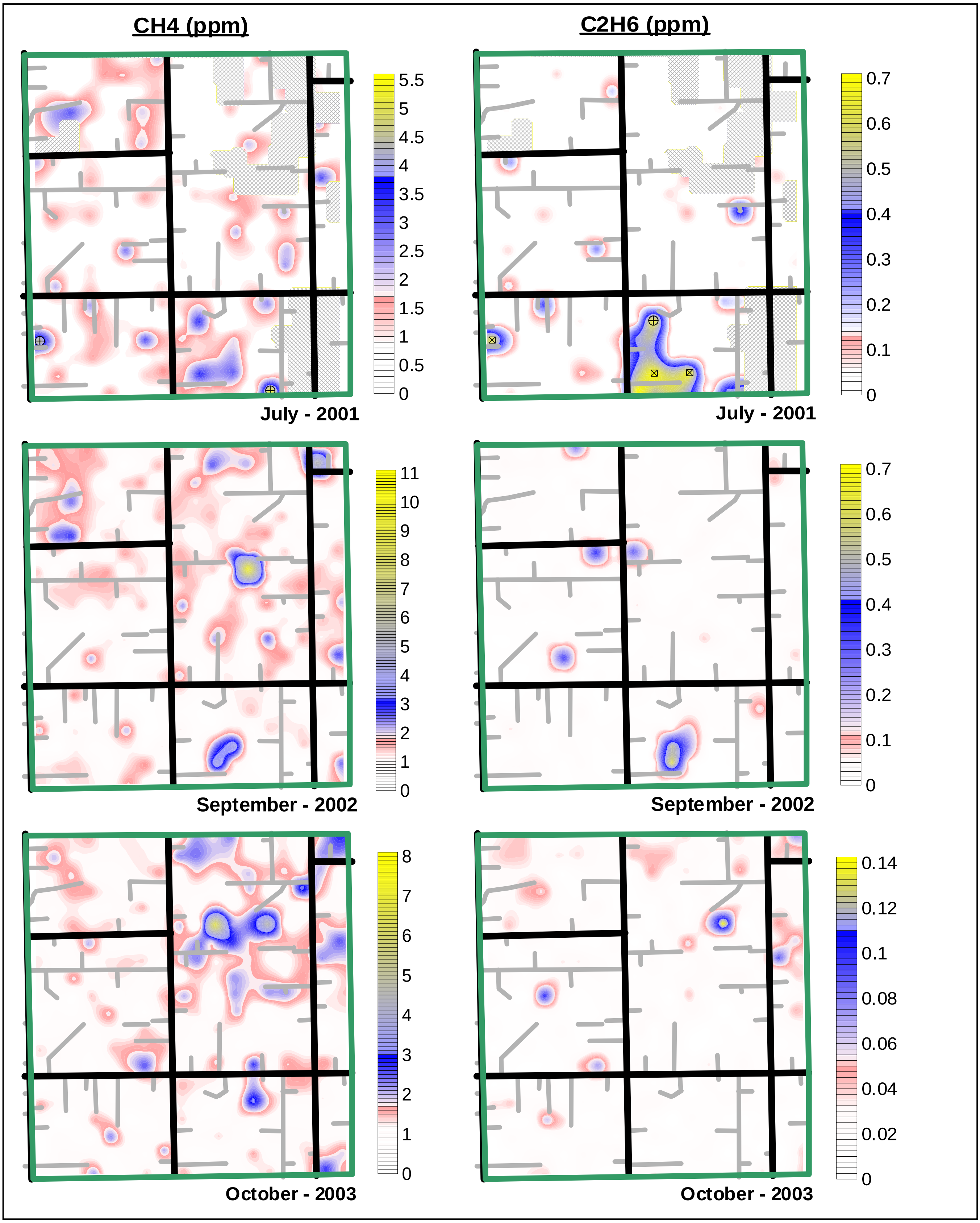


Figure 7 Contoured distribution of soil gas methane and ethane for the three sampling campaigns

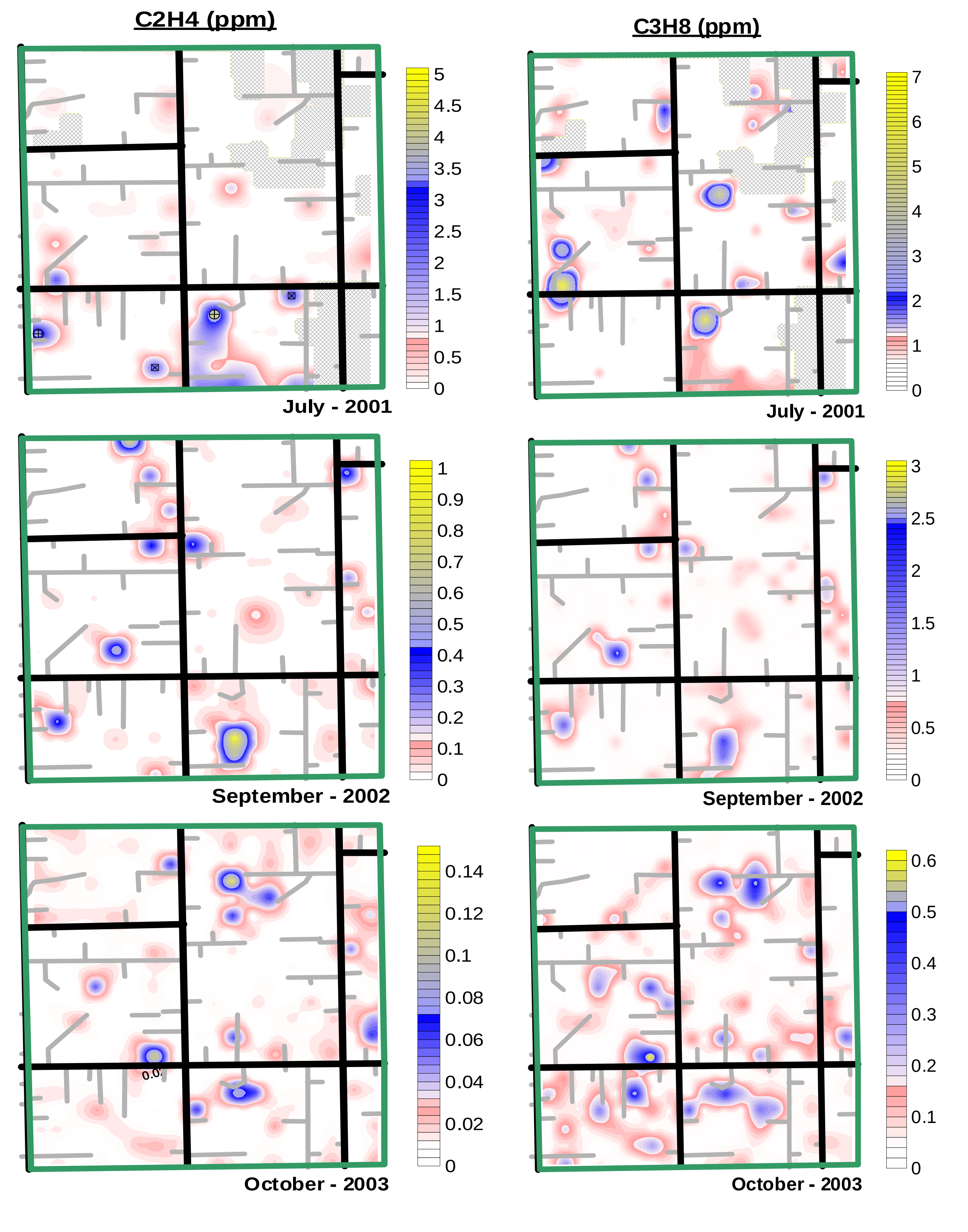


Figure 8 Contoured distribution of soil gas ethylene and propane for the three sampling campaigns

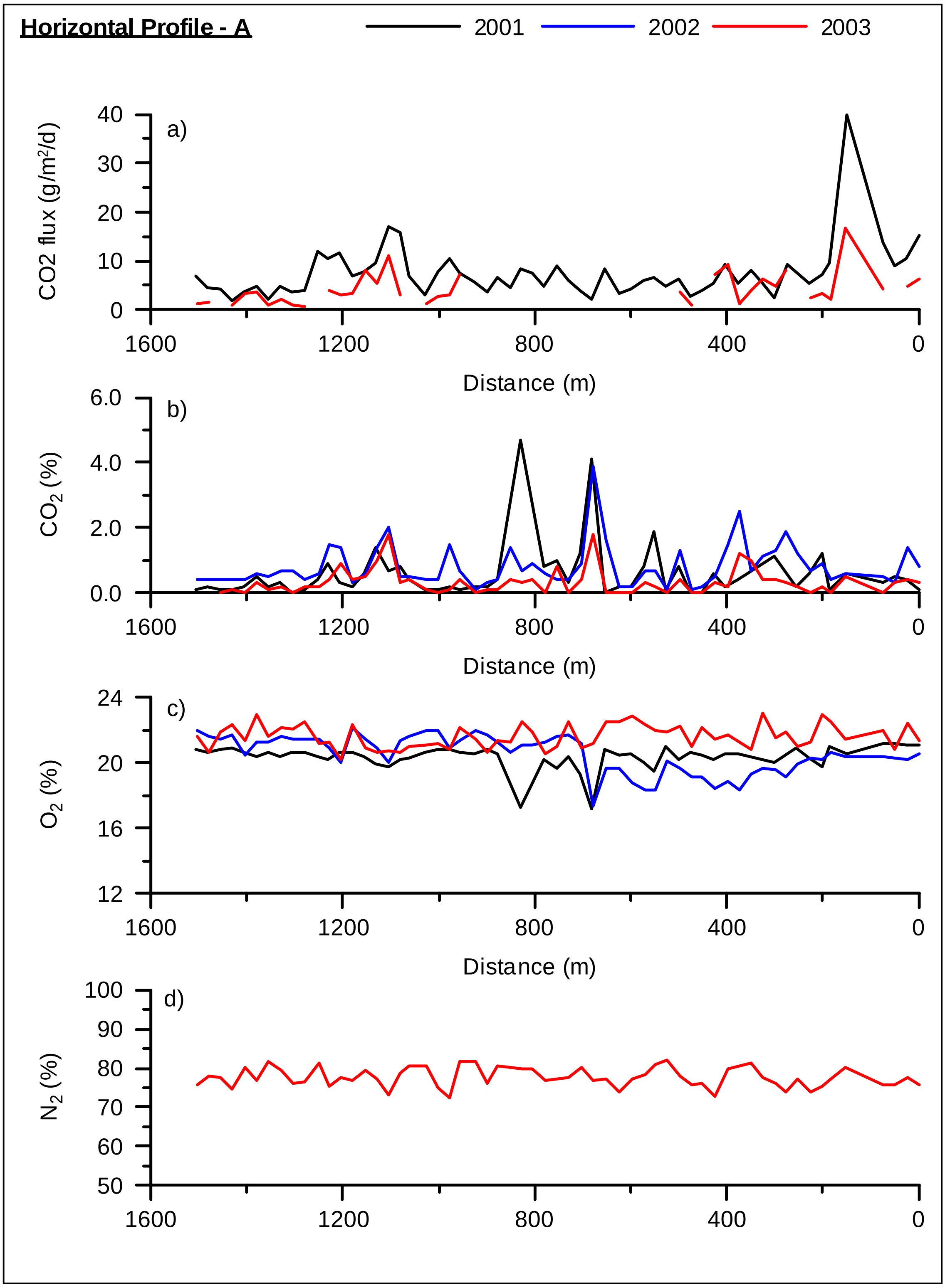


Figure 9 Horizontal profile A results.

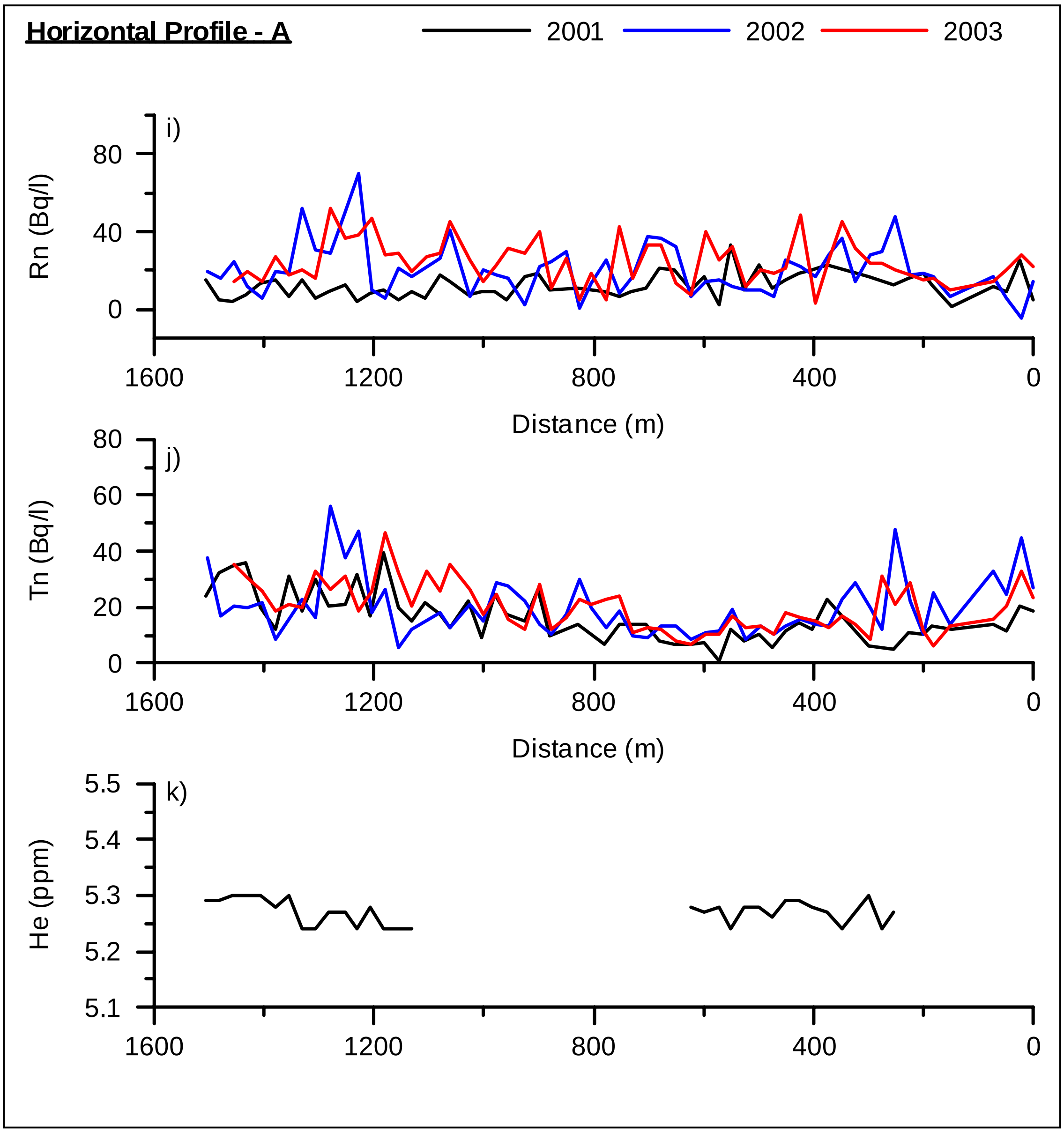


Figure 9 continued. Horizontal profile A results.

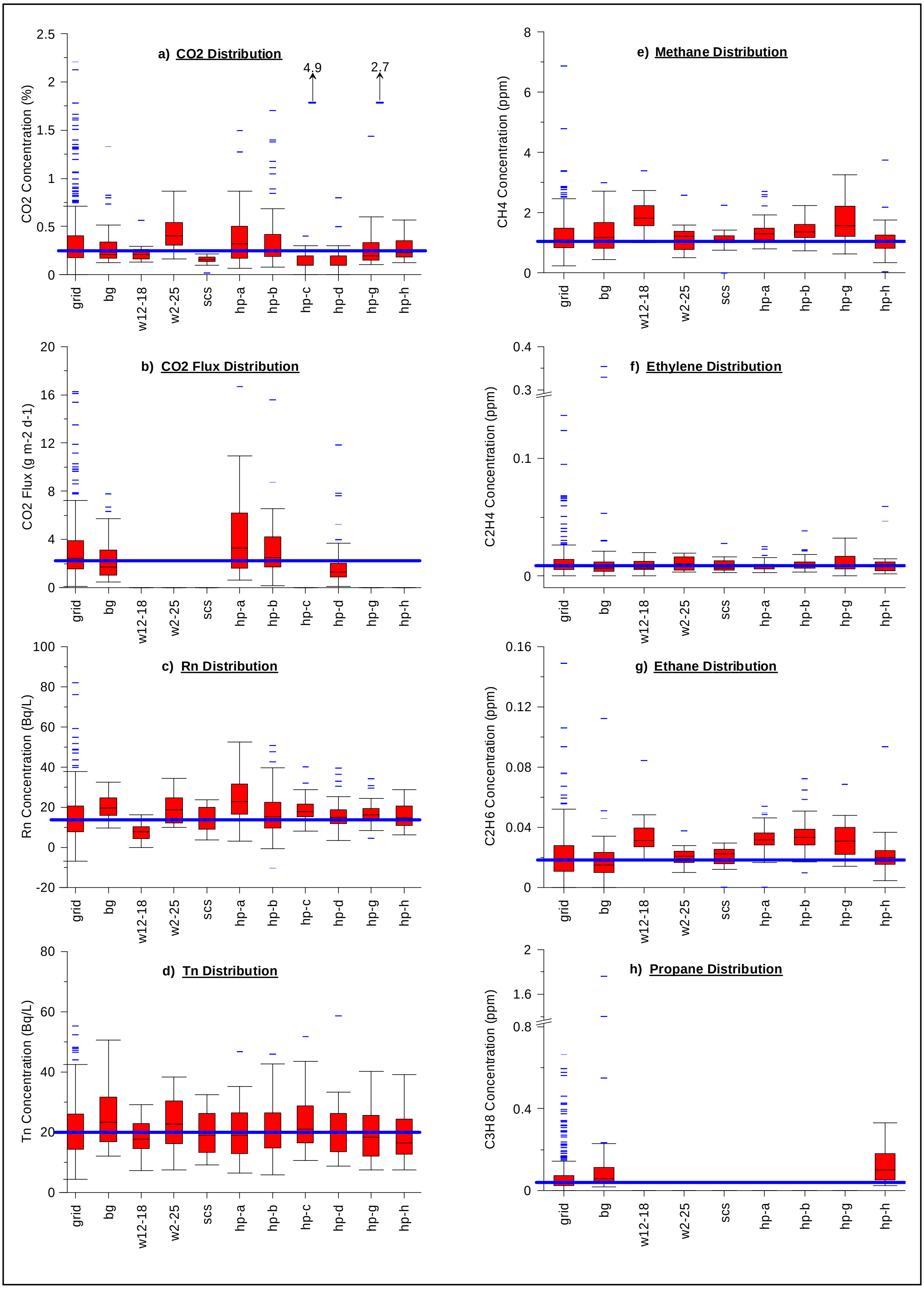


Figure 10 Box and whisker plots showing the statistical distribution of the various measured parameters for each of the 11 sites sampled during the October 2003 campaign. Note that the long horizontal blue line, which represents the median of the main grid data set, has been added to aid in comparisons.

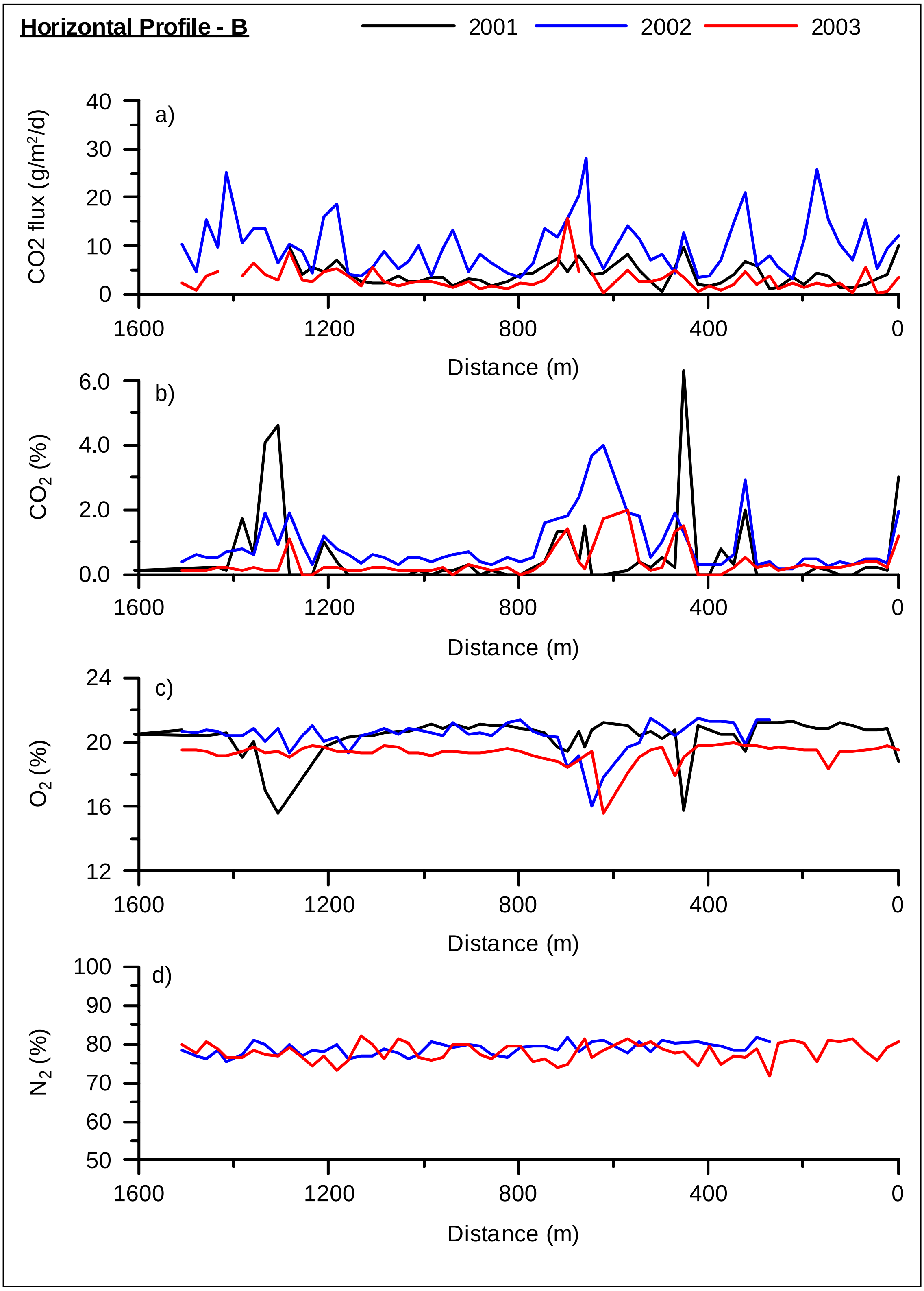


Figure 11 Horizontal profile B results

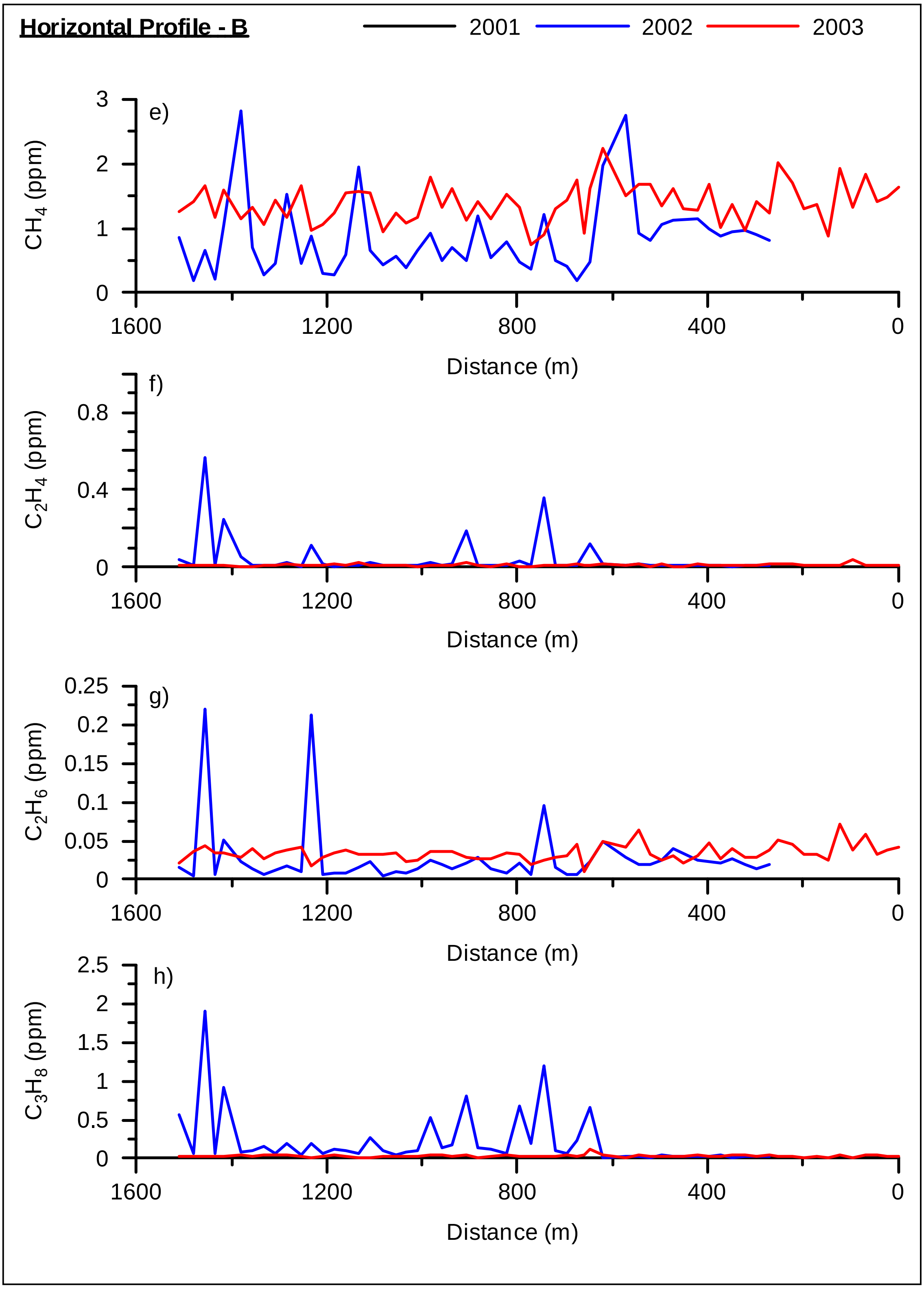


Figure 11 Continued. Horizontal profile B results

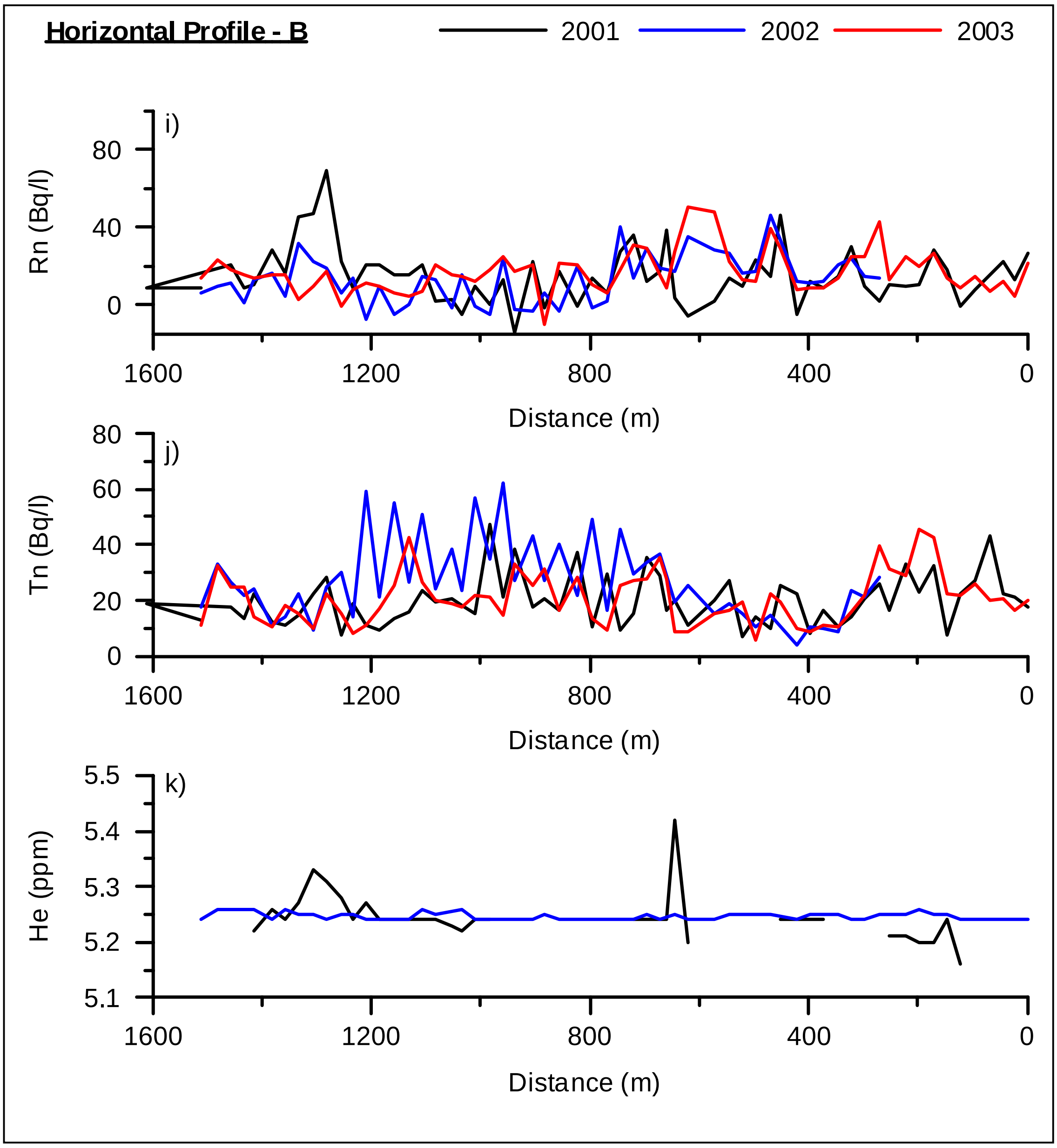


Figure 11 Continued. Horizontal profile B results

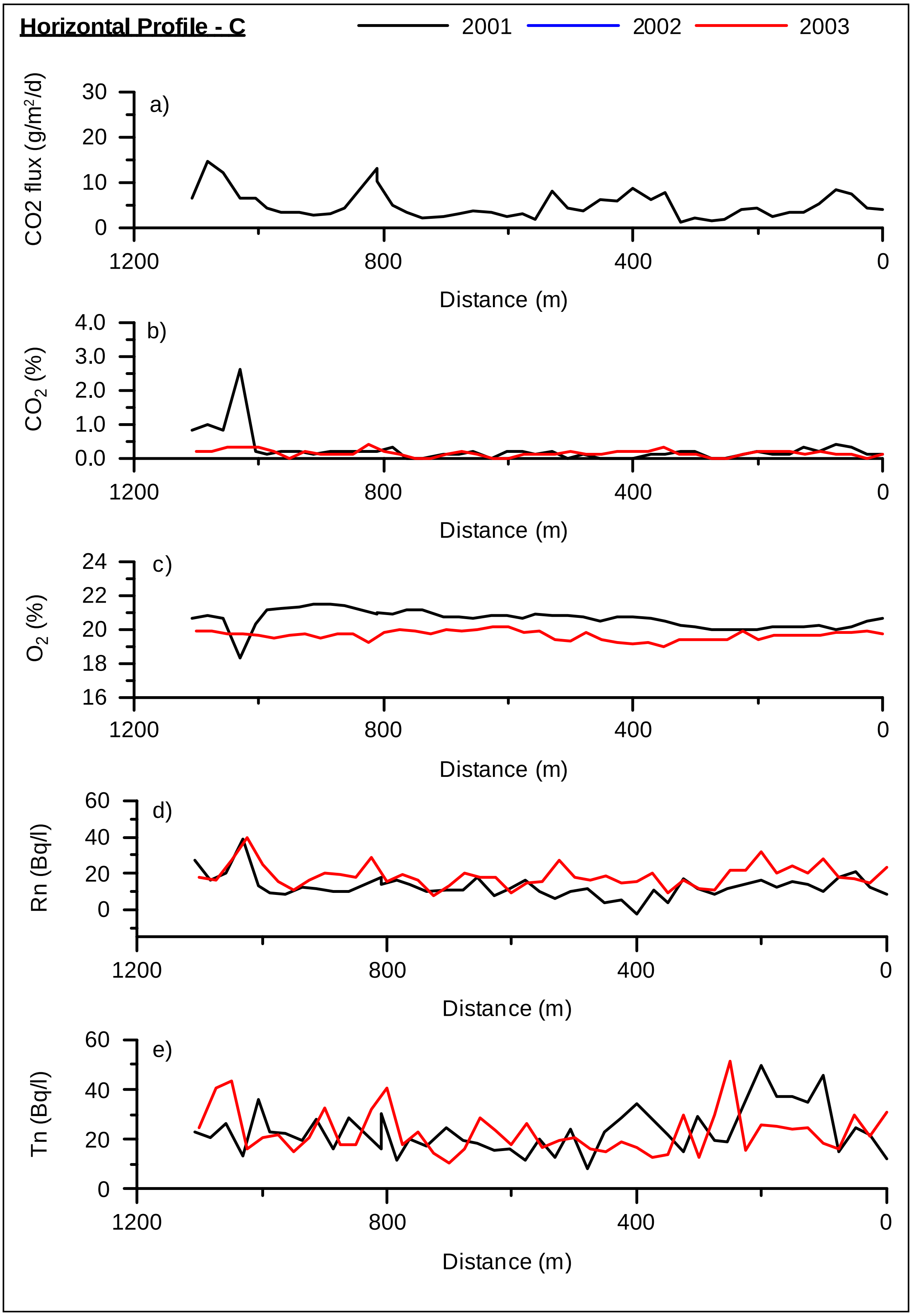


Figure 12 Horizontal profile C results.

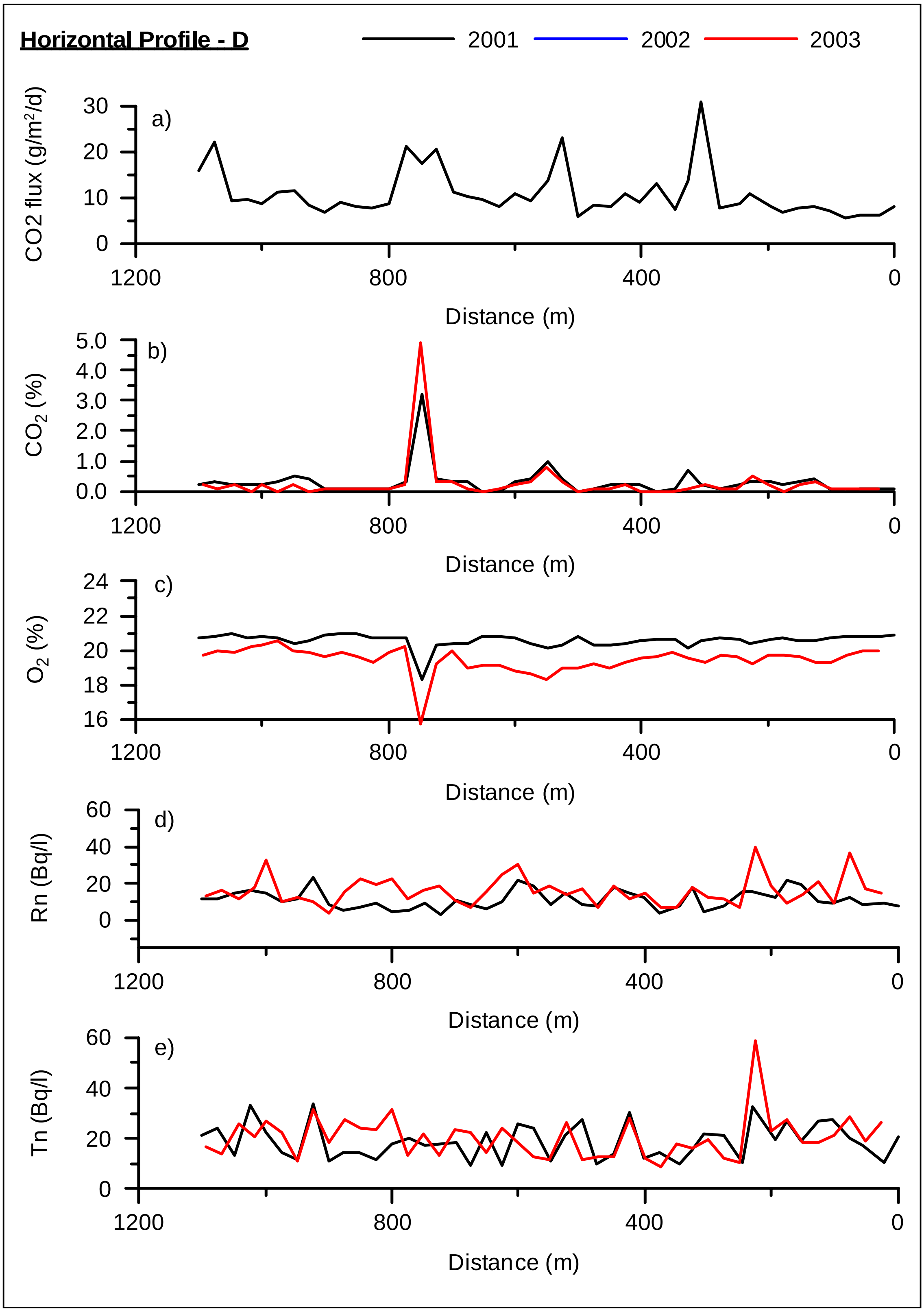


Figure 13 Horizontal profile D results

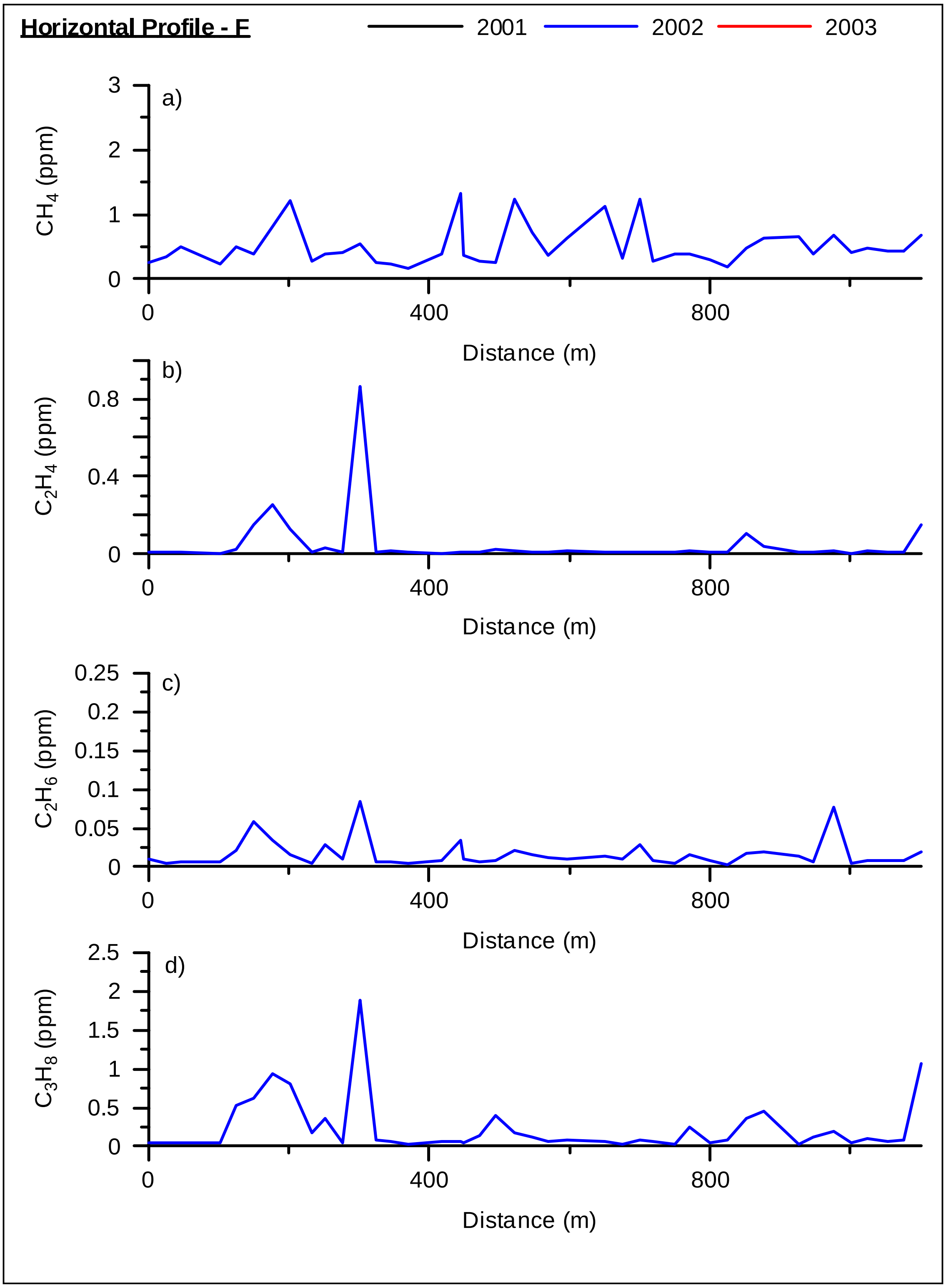


Figure 14 Horizontal profile F results.

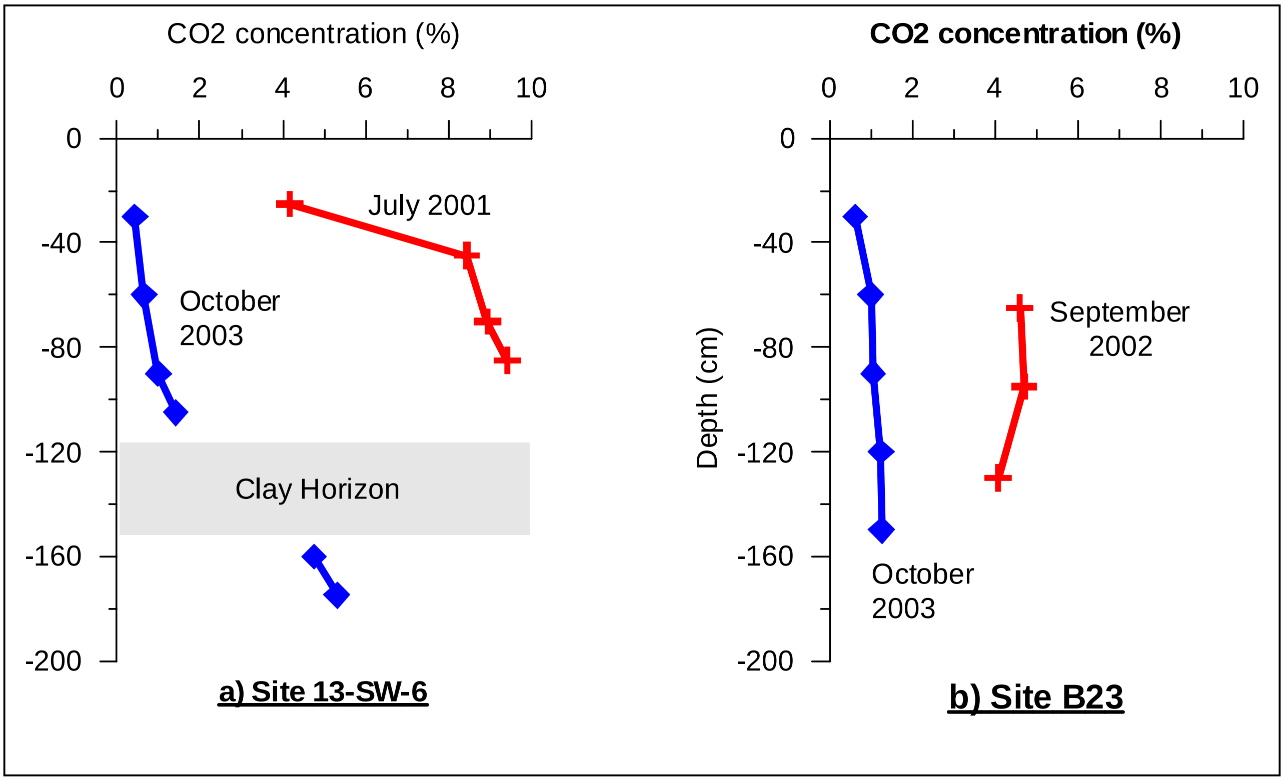
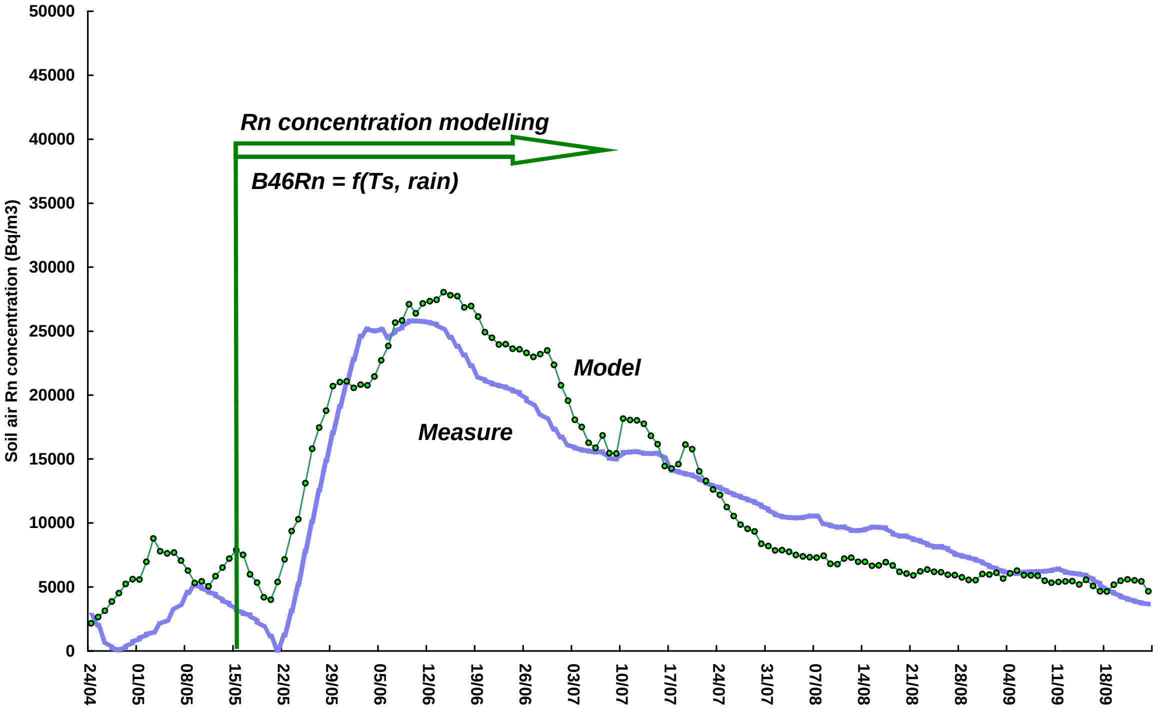
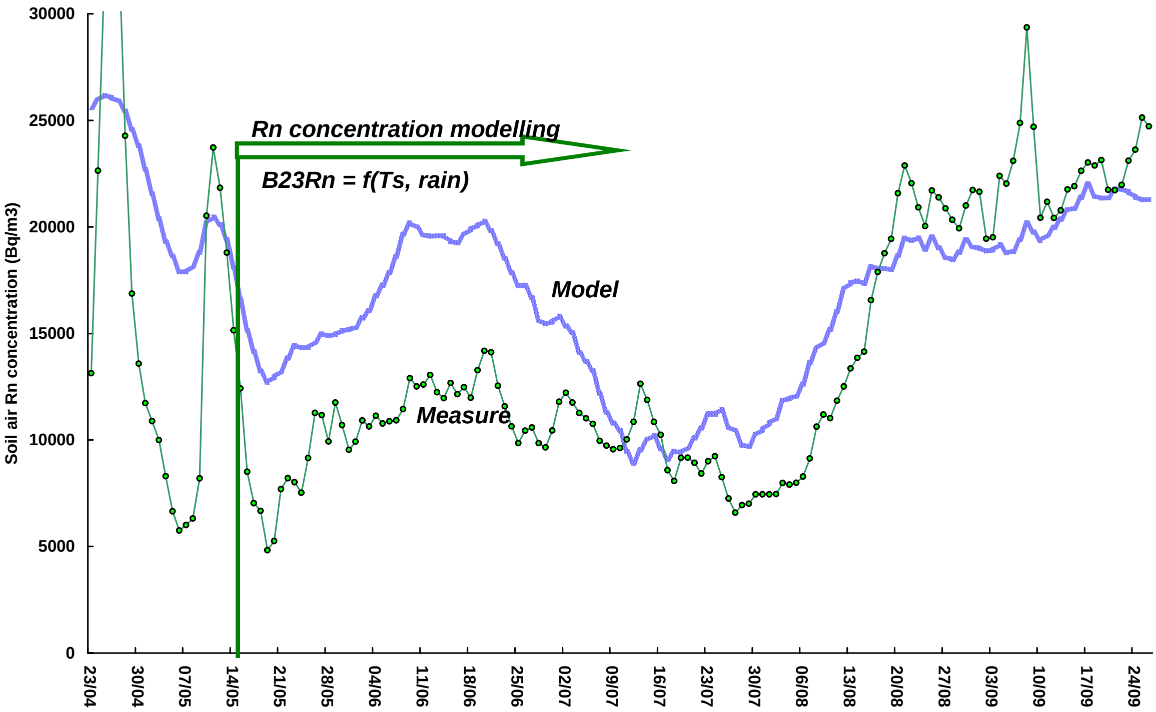


Figure 15 Soil gas CO_2 results from two of the six vertical profiles performed during the project. Note the relatively constant values below 40 cm, except for the two deep samples at site 13-SW-6 which are isolated below a low permeability clay horizon.

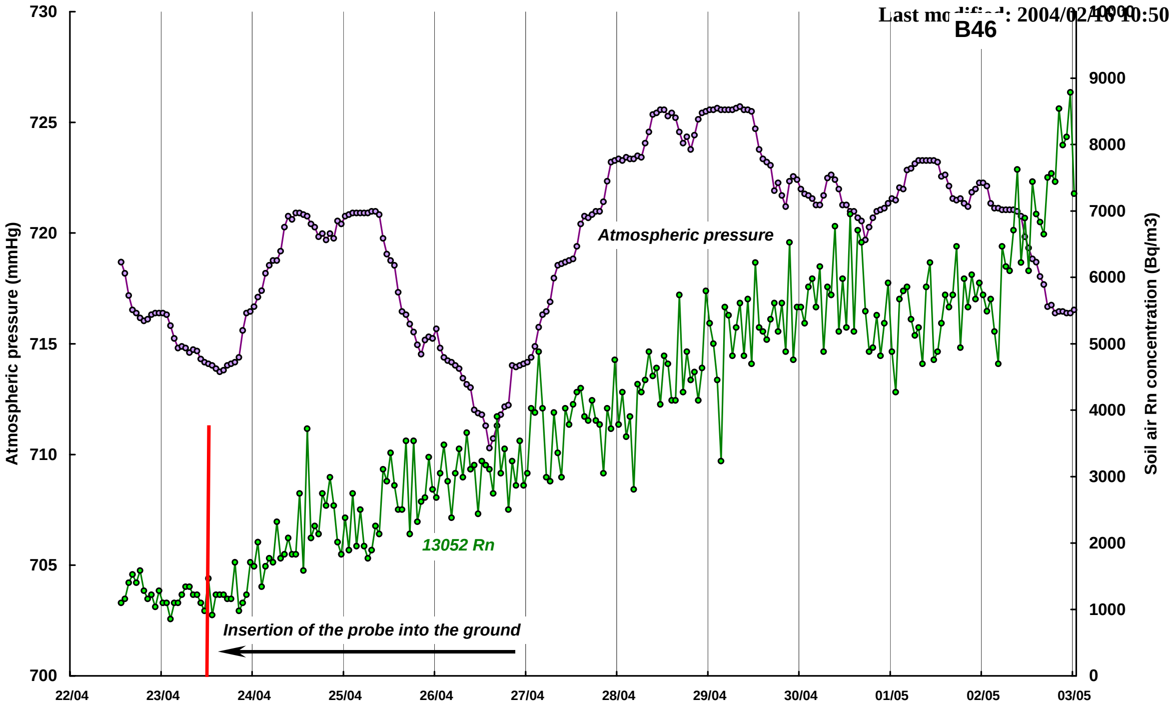


a)

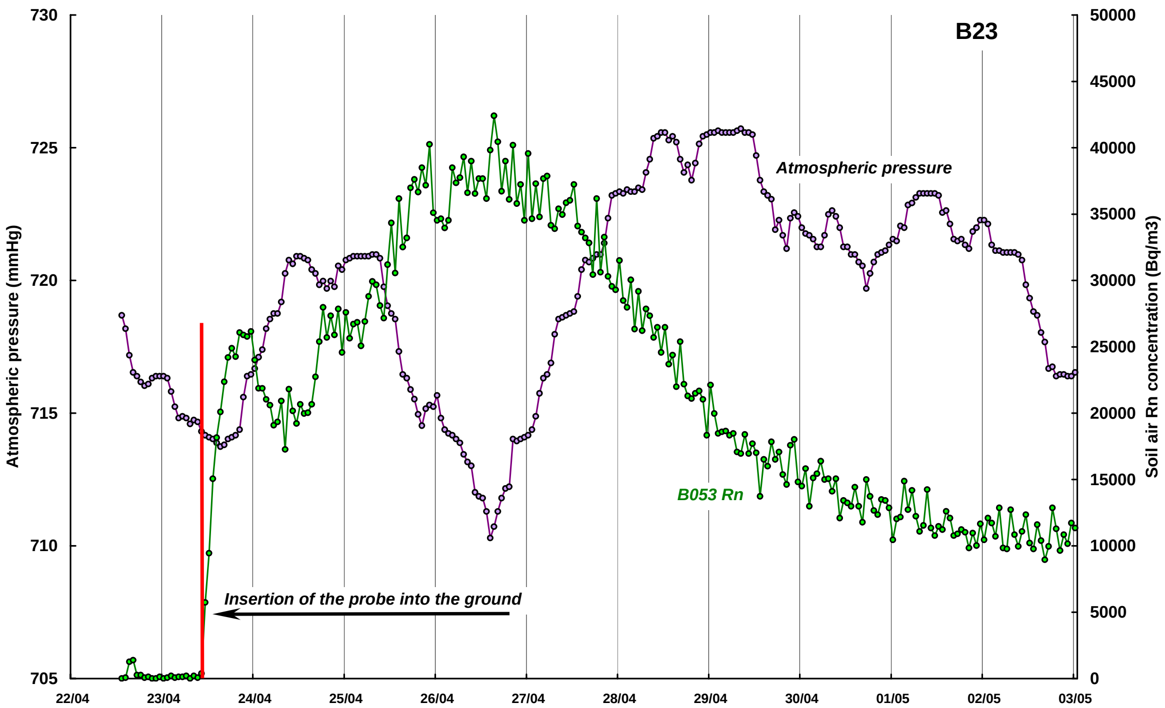


b)

Figure 16 Modelling of Rn concentration, from soil temperature and rainfall
a) Site B46; b) Site B23.



a)



b)

Figure 17 Example of increase of Rn concentration after the insertion of the probe into the ground a) when gas flow is driven by diffusion, site B46; b) when gas flow is driven by advection, site B23

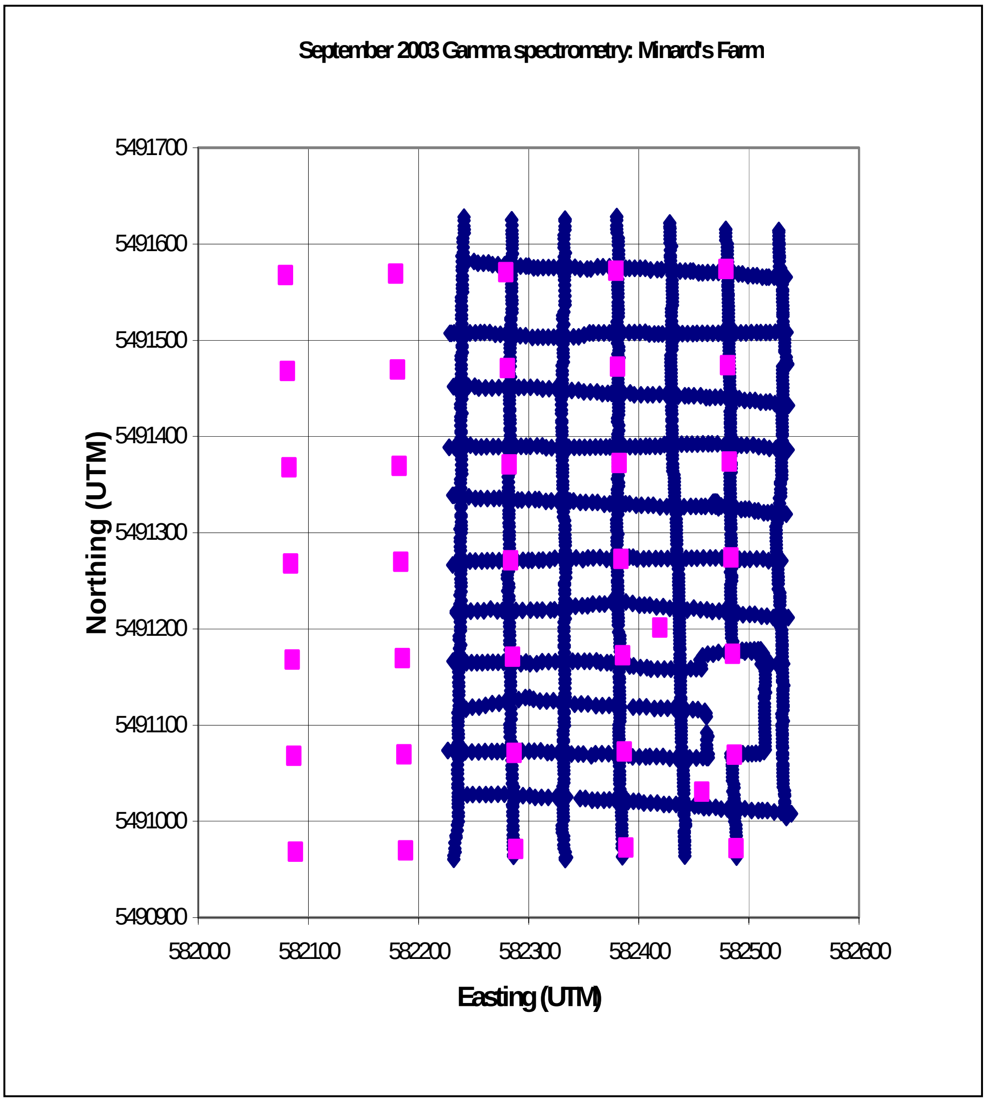


Figure 18 Gamma spectrometer traverses (black) and soil gas sample points (purple) for the background area near Minard's Farm

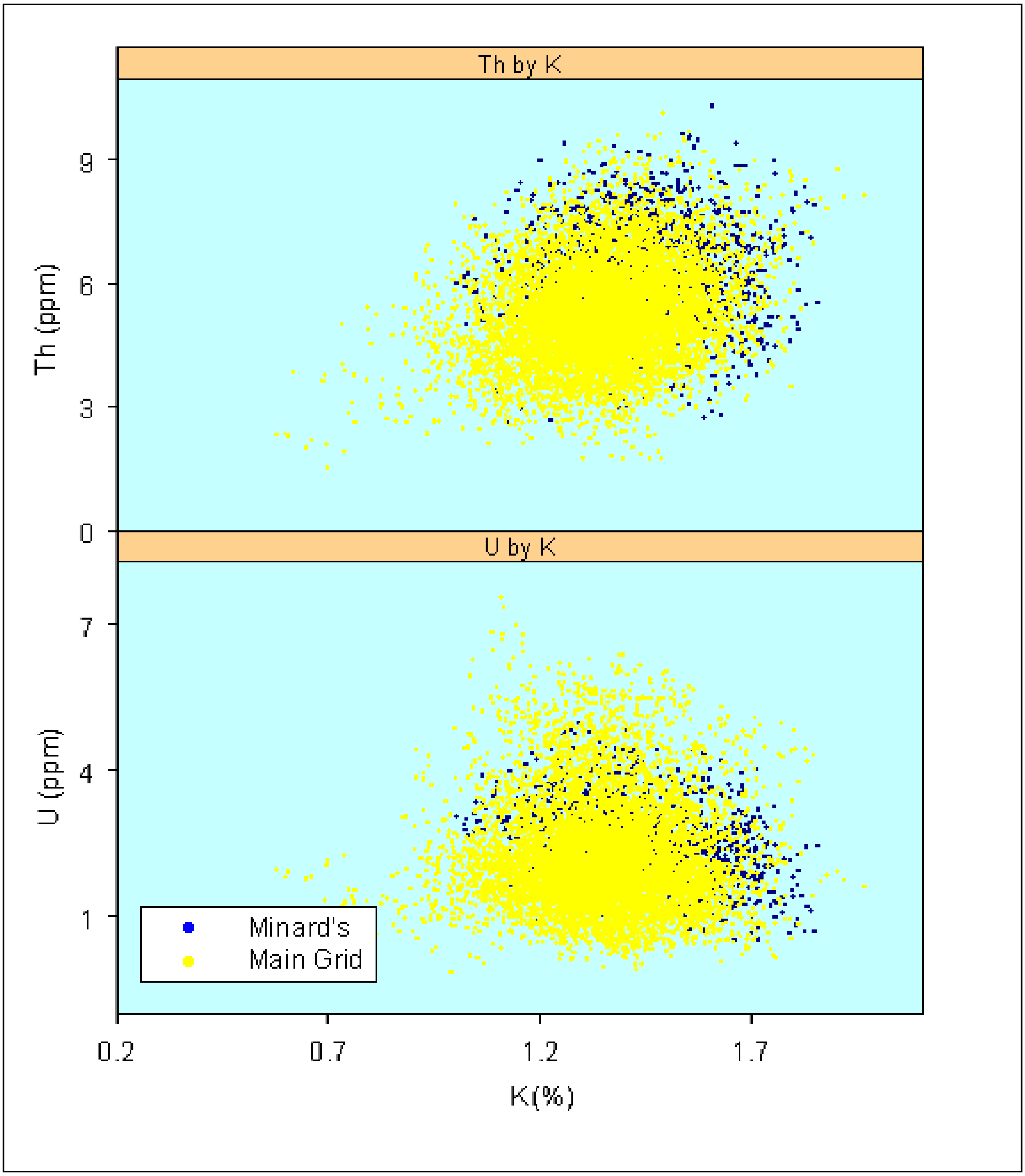


Figure 19 Comparison of gamma spectrometer data for the Background Site (Minard's Farm) and Main Grid areas

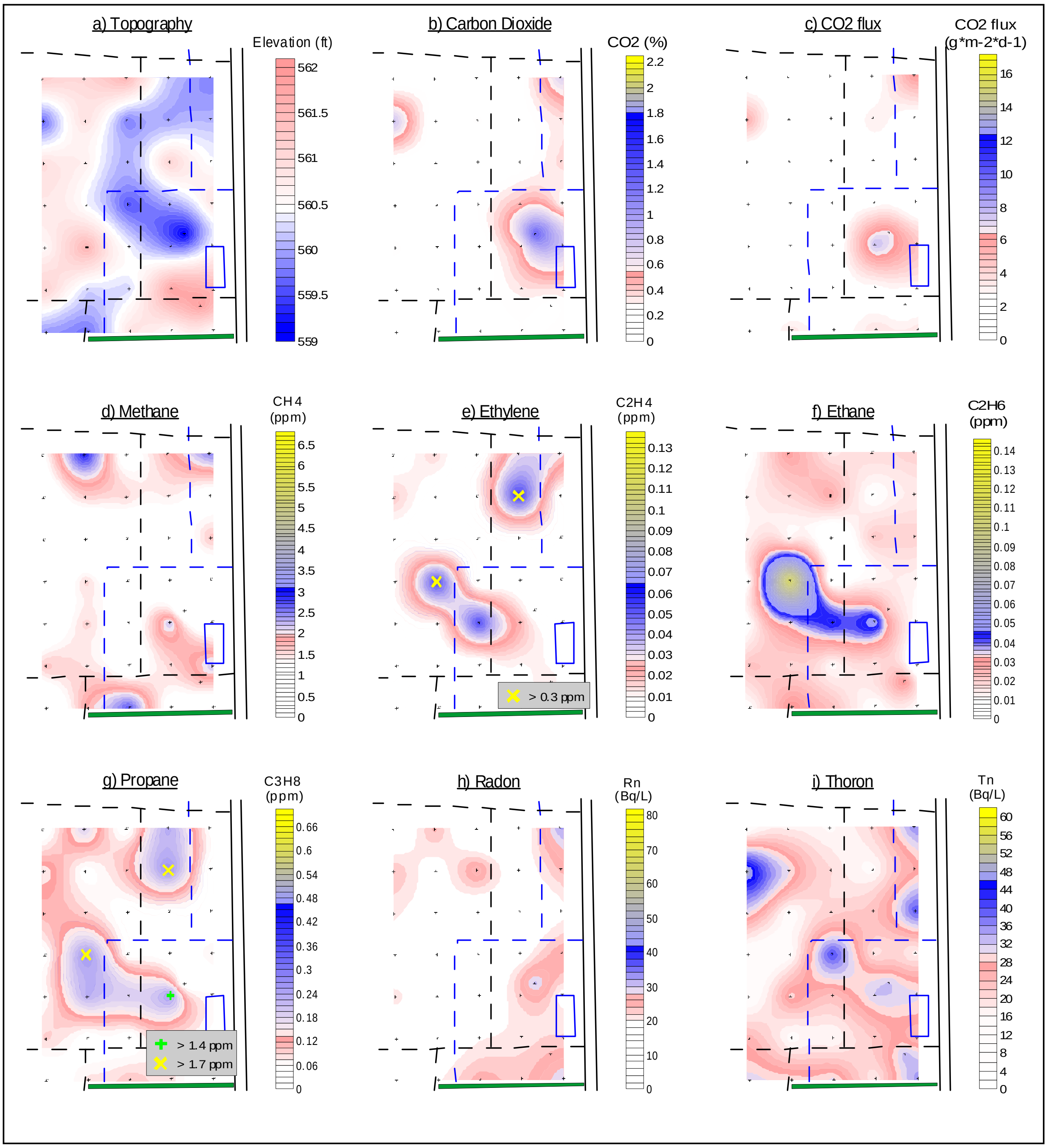


Figure 20 Contoured data for the background site. Note that the dashed blue lines are buried electrical lines, the black dashed lines are field boundaries, the blue rectangle is a dug-out, while the small plus signs are sample locations (approximately 100 m apart).

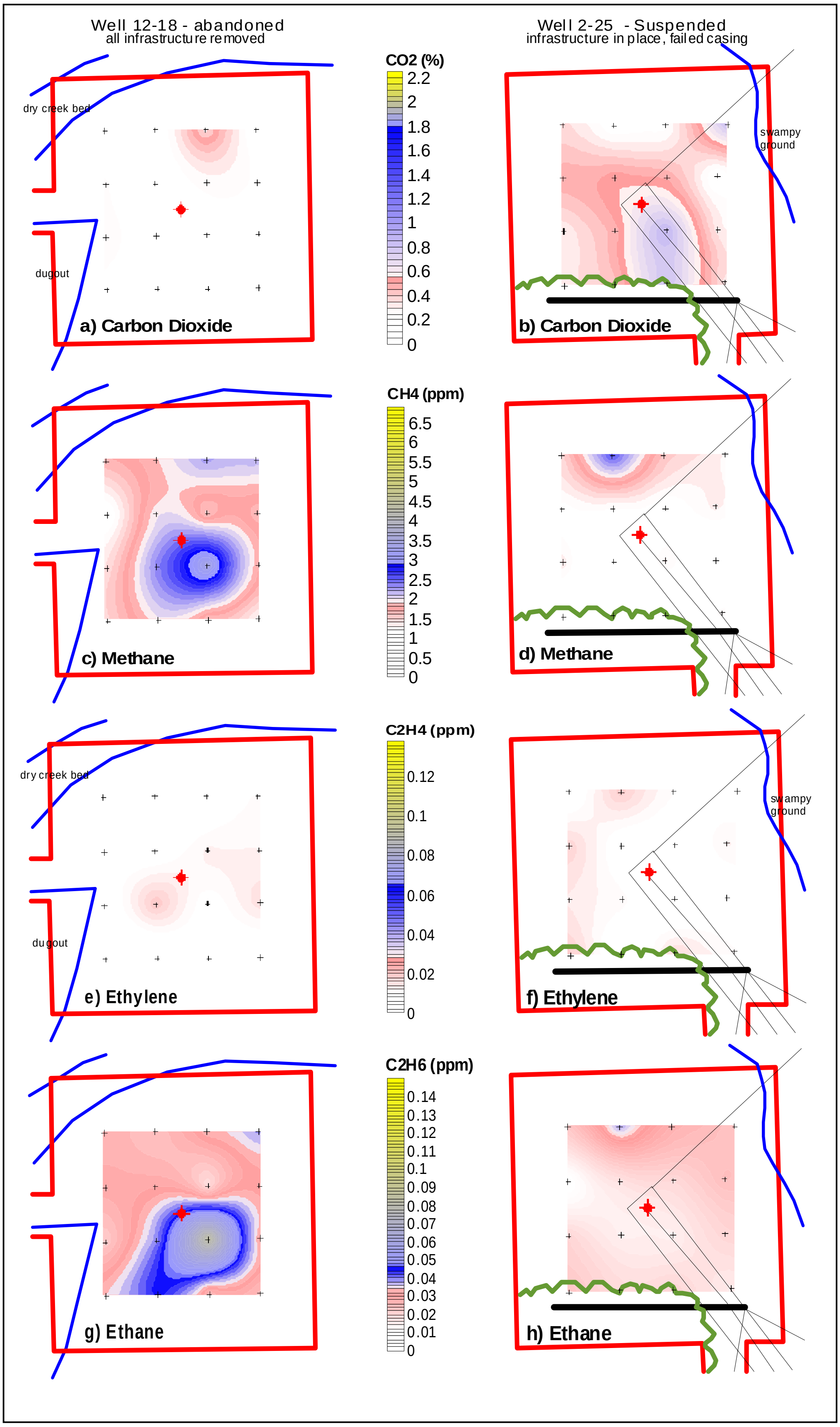


Figure 21 Contoured data for the two decommissioned wells. The one on the left is fully abandoned with all infrastructure removed (12-18) while the one on the right is suspended due to a failed casing (2-25). Note that the sample spacing, marked by the plus signs, is approximately 25 m. *Continued on next page*

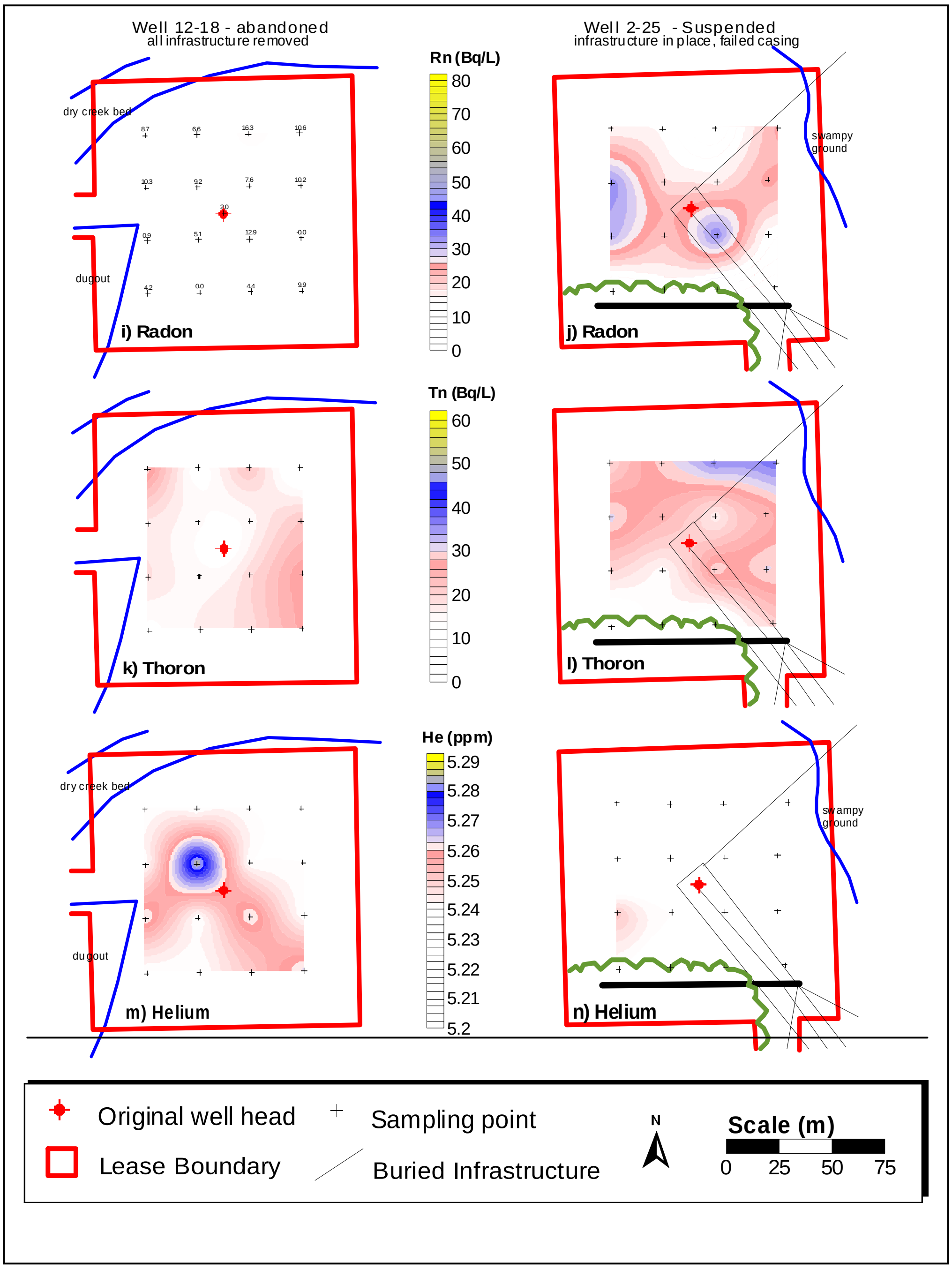


Figure 21. Continued. Contoured data for the two decommissioned wells. The one on the left is fully abandoned with all infrastructure removed (12-18) while the one on the right is suspended due to a failed casing (2-25). Note that the sample spacing, marked by the plus signs, is approximately 25 m

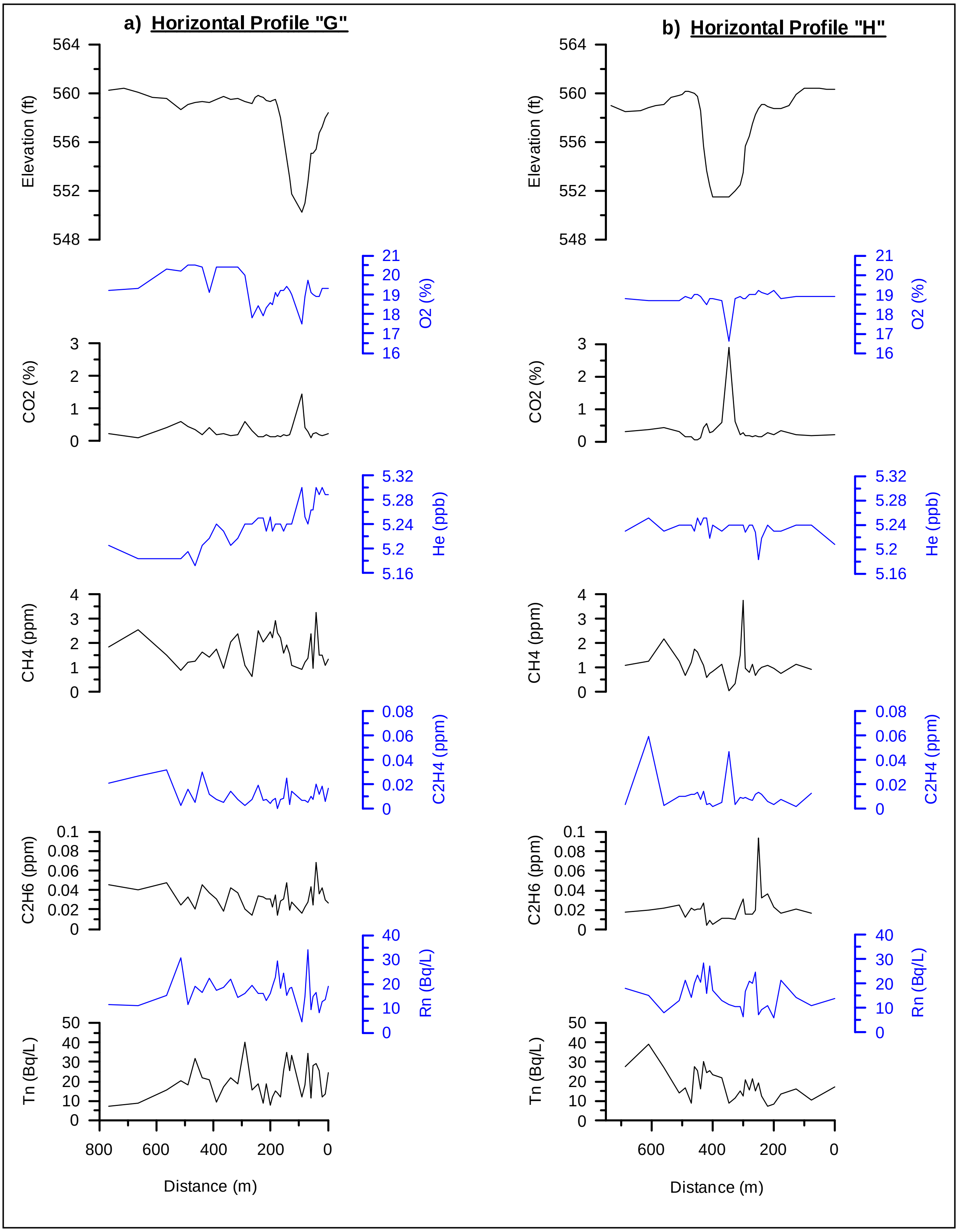


Figure 22 Results of horizontal profiles performed across a river lineament located to the north of the soil gas grid but within the CO_2 injection area.

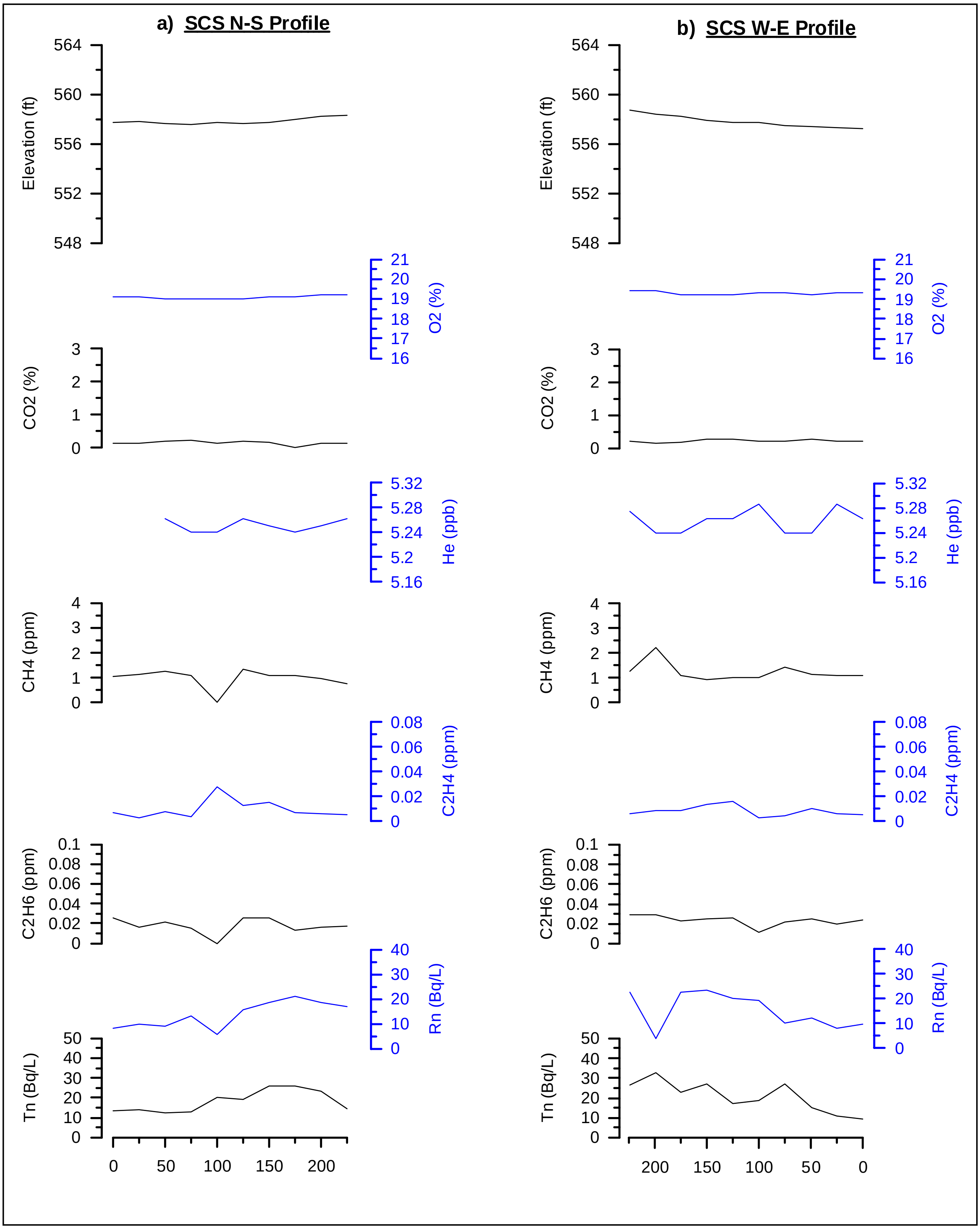


Figure 23 Results of the horizontal profiles performed across a salt collapse structure defined in seismic sections.

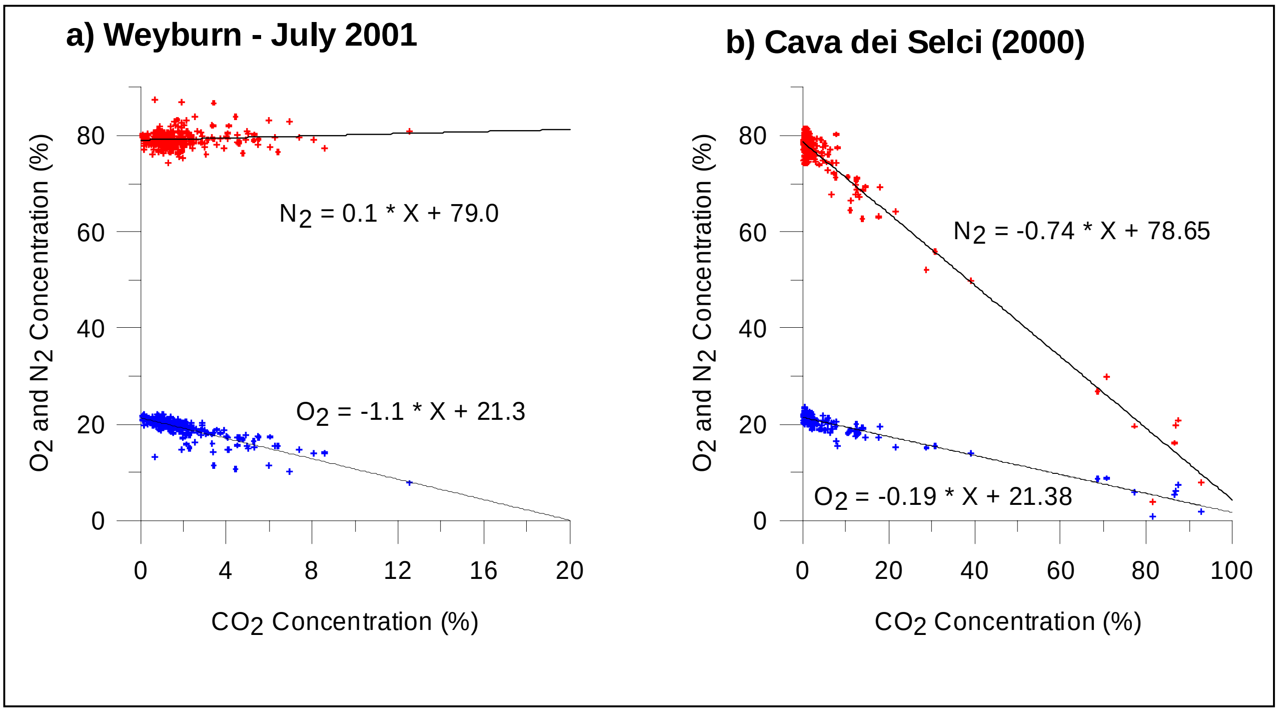


Figure 24 Plot showing the relationship between O_2 and CO_2 for the grid data set from Weyburn in July of 2001 as compared to data collected from Cava dei Selci in Italy, a dormant volcanic site which has known gas vents due to deep thermometamorphic reactions. As can clearly be seen the trend of the Weyburn data is towards a maximum value of 20% CO2, implying that there is a stoichiometric consumption of O_2 and production of CO_2. In contrast the Cava dei Selchi data trends towards a maximum of 100% CO_2, indicating that the CO_2 is coming from outside the shallow system and diluting the O_2, not consuming it.

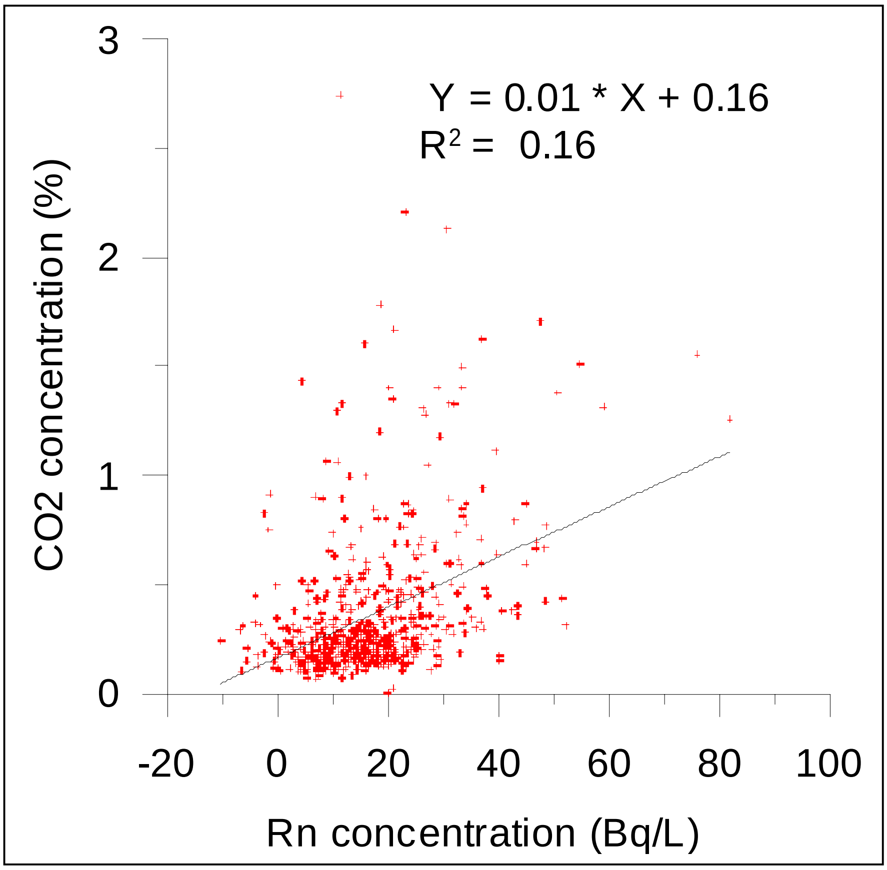


Figure 25. Data comparisons for Rn v CO_2