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Microseepage in drylands: Flux and implications in the global atmospheric source/sink budget of methane

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ABSTRACT

Drylands are considered a net sink for atmospheric methane and a main item of the global inventories of the greenhouse gas budget. It is outlined here, however, that a significant portion of drylands occur over sedimentary basins hosting natural gas and oil reservoirs, where gas migration to the surface takes place, producing positive fluxes of methane into the atmosphere. New field surveys, in different hydrocarbon-prone basins, confirm that microseepage, enhanced by faults and fractures in the rocks, overcomes the methanotrophic consumption occurring in dry soil throughout large areas, especially in the winter season. Fluxes of a few units to some tens of mg m^{-2} day^{-1} are frequent over oil–gas fields, whose global extent is estimated at 3.5–4.2 million km^2; higher fluxes (>50 mg m^{-2} day^{-1}) are primarily, but not exclusively, found in basins characterized by macro-seeps. Microseepage may however potentially exist over a wider area (~8 million km^2, i.e. 15% of global drylands), including the Total Petroleum Systems, coal measures and portions of sedimentary basins that have experienced thermogenesis. Based on a relatively large and geographically dispersed data-set (563 measurements) from different hydrocarbon-prone basins in USA and Europe, upscaling suggests that global microseepage emission exceeding 10 Tg $year^{-1}$ is very likely. Microseepage is then only one component of a wider class of geological sources, including mud volcanoes, seeps, geothermal and marine seepage, which cannot be ignored in the atmospheric methane budget.

1. Introduction

Dryland soil is considered a net biotic sink of atmospheric methane, with a global uptake on the order of 30 ± 15 Tg $year^{-1}$ (IPCC, 2001) or 20 ± 3 Tg $year^{-1}$ (Potter et al., 1996). There are however projections falling within the range of 5–58 Tg $year^{-1}$ (Dorr et al., 1993), indicating that there is still substantial uncertainty over the magnitude of this global sink. The negative gas flux, generally on the order of −5 to −1 mg m^{-2} day^{-1} (Dong et al., 1998), is due to methanotrophic oxidation by CH_4-consuming bacteria in the soil. Methanotrophic oxidation occurs in grassland, temperate and boreal forest soil, desert soils, fertilized soil, humisol, moss-derived peat soils, tundra soils and unflooded paddy soils (Minami and Takata, 1997). The soil is considered a source of methane only in wet conditions, in the presence of methanogenic bacteria (in all wetlands, including rice paddies, bogs and flooded soils; Batjes and Bridges, 1994).

In the 1980s and 1990s, some anomalies with respect to the expected dryland behaviour (i.e., positive fluxes instead of negative fluxes) were found in South America. Unexpected emissions of methane into the atmosphere (>1 mg m^{-2} day^{-1}) were found in two dry grasslands or savanna soils within the Orinoco Valley and in the Guyana Shield of northeastern Venezuela (Hao et al., 1988; Scharffe et al., 1990). These measurements were criticised and considered erroneous by other researchers, as the authors had no explanation for the positive methane flux (Crutzen, personal communication). Hao et al. (1988), however, suggested the possibility of gas release through upward diffusion from underground natural gas reservoirs near Chaguarama, which is in the region investigated. Hao et al. (1988) were quite right as their "biological" survey was actually conducted over what some years later would be recognized as one the largest petroleum systems in the world (the Orinoco Petroleum Belt; Erlich and Barrett, 1992). The area investigated by Scharffe et al. (1990), near the Guri dam, south of the Orinoco Belt, is located in association with important SW–NE deep fault systems containing highly fractured and permeable mylonites, characterising the regional brittle tectonics of the Guyana Shield (Bellizzia et al., 1976). This location apparently has deep-sourced gas migration processes operating.

Later, positive fluxes of methane in dry lands were reported in several sites in the USA in the framework of studies on hydrocarbon seepage from sedimentary basins (Klusman et al., 1998, 2000a). Indeed, the occurrence of methane and light alkane anomalies in dry soil has been extensively used by geologists and geochemists as a

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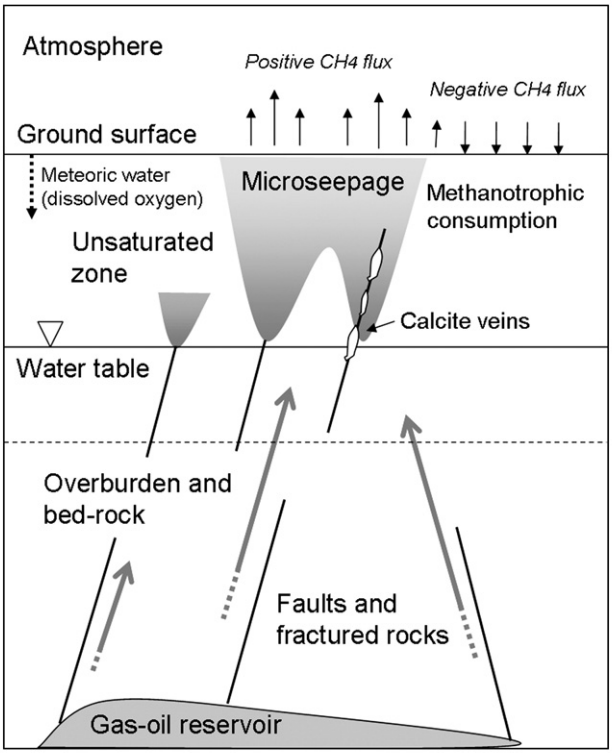

Fig. 1. Sketch of the microseepage process, from a hydrocarbon reservoir, through the unsaturated zone, to the atmosphere.

tool for oil and gas exploration since 1930s (Laubmeyer, 1933; then, more recently: Jones and Drozd, 1983; Davidson, 1986; Schumacher and Abrams, 1996; Klusman, 1993; Tedesco, 1995; Hunt, 1996; Matthews, 1996; Schumacher and LeSchack, 2002; Abrams, 2005). Indirect methods, such as microbial prospecting (e.g., Tucker and Hitzman, 1996; Wagner et al., 2002), remote sensing (e.g., Van der Meer et al., 2002) and magnetic measurements (e.g., Liu et al., 2004) have also shown the existence of microseepage throughout large areas over oil–gas fields on various continents. Nevertheless, these studies focused exclusively on the detection in the soil of anomalous concentration of methane and light alkanes (and associated geophysical or geochemical indicators); the soil–atmosphere flux measurement, being not necessary for oil/gas exploration, was never carried out. Understanding the impact on the atmosphere was not an objective. Consequently the available data-set on microseepage flux is rather poor. Only recently, since 2002, a large number of flux data have been acquired throughout dry soil areas in hydrocarbon-prone sedimentary basins of Europe and Asia, specifically in Italy, Romania, Greece, Azerbaijan and China (Etiope et al., 2002; Etiope et al., 2004a,b; Etiope et al., 2006; Tang et al., 2007; Tang et al., 2008). These surveys and the US surveys performed by the Colorado School of Mines (e.g., Klusman, 2006; and references therein) form the only systematic programme of measurements of microseepage flux to the atmosphere.

Today, it is known that the positive flux of methane, or microseepage, can reach levels of tens, hundreds and thousands of mg m^{-2} day^{-1} throughout large areas, especially around macro-seeps such as occur associated with mud volcanoes (Etiope et al., 2004a,b; Etiope and Milkov, 2004). At lower rates, microseepage is quite common and pervasive within petroliferous and sedimentary basins.

Finally, positive fluxes of methane from the soil can also occur in geothermal areas (Hernandez et al., 1998; Etiope, 1999; Klusman et al., 2000b; Etiope et al., 2007a), where methane is produced by high temperature inorganic reactions (Etiope and Klusman, 2002).

All these facts pose some key questions:

1) Has the occurrence of microseepage ever been considered in the estimates on global soil sink?
2) How large is the dryland area potentially affected by microseepage?
3) How large is the global microseepage emission into the atmosphere?
4) What are the implications on the global greenhouse gas budget?

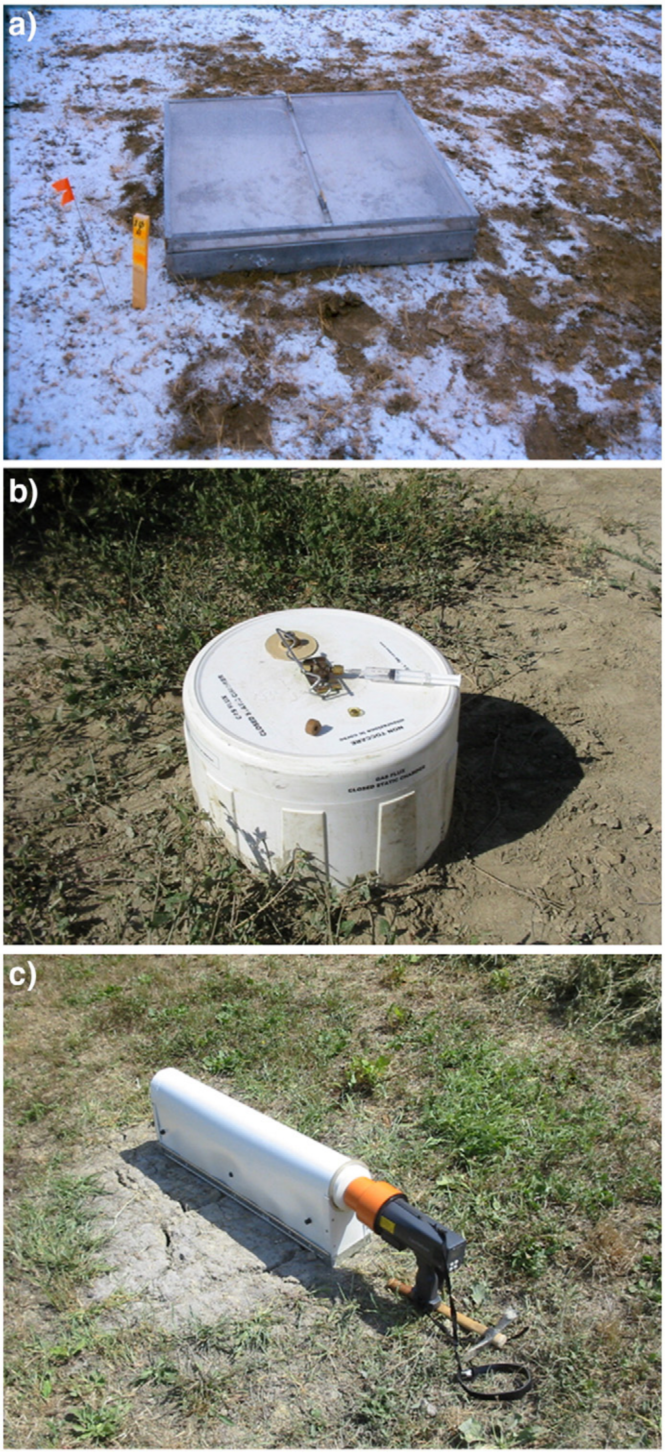

Fig. 2. Photos of the closed-chamber systems used in microseepage surveys in USA (a) and Europe (b, c). Methane concentration increase is measured by GC analysis of samples taken manually by syringes (a, b) or by direct detection by laser sensor (c).

This work will try to provide answers to these questions, with the support of a review of available literature data and new key data-sets acquired in petroliferous areas in the USA and Italy.

2. Has the occurrence of microseepage been considered in the estimates on global soil sink?

The answer is no. Thus far, microseepage has not been considered in any agro-environmental study as a possible methane source from the soil. The global estimates of the soil uptake are usually made by process-level models or by multiplying averages of chamber measurements for various ecosystem types by estimates of the area covered by each ecosystem (Potter et al., 1996). Field measurements are actually limited to small areas, assuming that the average measured flux value is representative of the ecosystem investigated; individual global ecosystem areas, to which field data are extrapolated, are in the order of units and tens of 10^6 km^2. The global dryland area is about 54.1×10^6 km^2, i.e., 40% of the world's land area (Potter et al., 1996).

Process-level models are based on downward diffusion of gas from the atmosphere into the top 30–50 cm of the soil, and on the soil properties. Recent data suggest that in more permeable semi-arid soils, oxygen penetration from the atmosphere allows some methanotrophic oxidation to occur at greater depths (Klusman, 2003a, 2006). The possibility of upward diffusion or advection of gas from the subsoil has never been considered. Basically, the global methane uptake in the soil is derived by assuming, *a priori*, that in presence of methanotrophic bacteria in an oxydising environment, methane sources other than the atmosphere do not exist. Indeed, this is not the case, as indicated by thousands of methane and light alkane concentration measurements, and flux anomalies reported in the course of exploration and environmental surveys in dry soils over hydrocarbon-prone sedimentary basins. Still today the international community of soil and atmosphere chemistry is not aware of the possibility of microseepage in drylands (as discussed in the 5th Symposium on Non-CO$_2$ Greenhouse Gases, Wageningen, July 2009). New initiatives should be promoted for reviewing and re-assessing, with a broad multidisciplinary approach, the role of soil in the global methane budget.

3. How large is the dryland area potentially affected by microseepage?

As described by Brown (2000) and Etiope and Klusman (2002) microseepage is the slow, continual loss of CH$_4$ and light alkanes from depths of 2–5 km in sedimentary basins where thermal degradation of indigenous organic matter is occurring (Fig. 1). Microseepage is basically a pervasive, diffuse exhalation of methane from soil resulting from natural gas migration from underground hydrocarbon reservoirs. It is assumed that microseepage is a general phenomenon driven by buoyancy of the gas phase relative to connate waters (Price, 1986; Klusman, 1993); frequently, gas migration can be considered in terms of microbubbles, bubbles and slug flows along faults and fractured rocks (Etiope and Martinelli, 2002). It is evident that microseepage is enhanced by the presence of faults and fractures, especially those produced by neotectonics (Klusman, 1993; Etiope, 1999). Fig. 1 is a schematic of a model for microseeping gases passing from the hydrocarbon reservoir, through the saturated zone into the unsaturated zone, and then into the atmosphere. Methanotrophic oxidation can partially attenuate the microseepage, which over a long time frame can produce calcium carbonate veins and dispersed calcium carbonate of distinct isotopic composition.

More than 75% of the world's petroliferous basins contain surface macro-seeps (Clarke and Cleverly, 1991). There is evidence that, at least in some regions, the gas flux from seeps decreased after petroleum was extracted from nearby reservoirs (Etiope et al., 2008b). A large number of surface gas or oil manifestations from the Alpine-Himalayan, Pacific Ocean and Caribbean sedimentary belts, described in the 20th century's petroleum geology literature (e.g., Link, 1952; Macgregor 1993; Hunt, 1996) have now disappeared or are greatly diminished. Consequently also microseepage should have

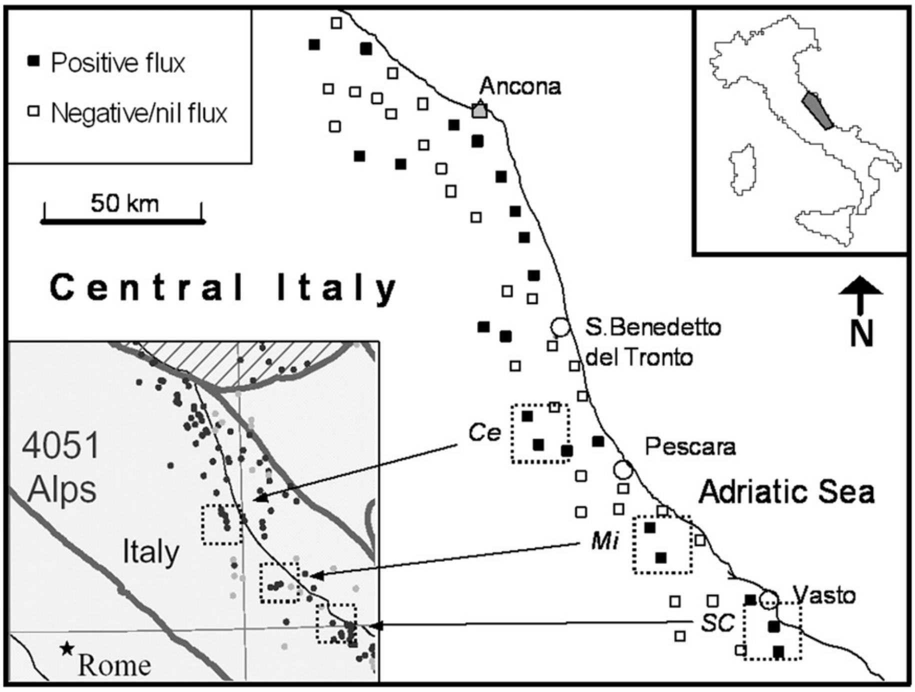

Fig. 3. Reconnaissance microseepage survey in the hydrocarbon basin along the Adriatic coast in central Italy. Black squares are the sites where positive fluxes of methane from the soil have been detected. Negative or nil fluxes were detected in the white squares. Bottom-left corner: distribution of oil and gas fields. Hatched squares mark the main oil–gas fields of the region (Ce: Cellino gas field; Mi: Miglianico oil field; SC: S.Salvo Cupello gas field).
Extracted from the USGS map compiled by Pawlewicz et al., 2001.

diminished; but many measurements are proving that, even in areas of "dead" macro-seeps, microseepage is still active.

Klusman et al. (1998, 2000a) assumed that potentially microseeping areas include all the sedimentary basins in a dry climate, with petroleum and gas generation processes at depth. This area has been estimated to be 43.4×10^6 km^2, which is less than the 54.1×10^6 km^2 of Potter et al. (1996) for the area of dry climate.

The flux data available today suggest that microseepage corresponds closely to the spatial distribution of hydrocarbon reservoirs, coal measures, and portions of sedimentary basins that are, or have been in the past, at temperatures >70 °C (thermogenesis). Accordingly, Etiope (2005) assumed that microseepage may occur within the so-called Total Petroleum System (TPS), a term used in petroleum geology (USGS, 2000) to describe the whole hydrocarbon-fluid system in the lithosphere including the essential elements and processes needed for oil and gas accumulations, migration and seeps. In the TPS, the gas migration to the surface can occur by advective mechanisms (Brown, 2000; Etiope and Martinelli, 2002), driven by two main factors: excessive pressure gradients in the rocks and permeable pathways (fractures, faults and permeable sedimentary horizons); wherever both factors exist, microseepage to the surface can result.

In the world, 42 countries produce 98% of the petroleum, 70 countries produce 2%, 70 countries produce 0%. So a TPS, and consequently the potential for microseepage, occur in 112 countries. This first consideration suggests that microseepage is potentially a very common phenomenon and widespread on all continents. Based on a careful analysis of onshore TPS map and GIS data-sets (USGS, 2000), the global area of potential microseepage has been estimated in the order of 8×10^6 km^2 (Etiope, 2005); this area might exclude wide zones of coal measures and portions of sedimentary basins that experienced thermogenesis. It is almost twice the global wetland area (Matthews and Fung, 1987) and about 15% of the global dryland area. It must be emphasized that this estimate refers to the potential area of microseepage. The actual microseepage area can be significantly smaller.

In the next sections, two cases of microseepage in petroliferous basins are discussed: the first in an area characterized by small and often inactive macro-seeps (central Italy, Adriatic coast); the second in sedimentary basins, with and without oil–gas fields, and with lower rates of seepage (Colorado, Nevada, Utah and Wyoming, USA). In both areas, we examine first the occurrence of microseepage (in terms of gas anomalies in the atmosphere and soil profiles; Section 3.1); then we report the fluxes observed (Sections 4.1 and 4.2).

3.1. First surveys on microseepage extent within petroliferous basins

Accurate surveys, in progress in Italy, Greece, Romania and in the United States, are trying to estimate the actual extent of microseepage within a TPS. Most of the surveys are carried out by using traditional techniques (closed chamber and gas-chromatography; e.g., Klusman, 2003a; Etiope et al., 2004a; Fig. 2), extensively employed in agro-environmental and biogeochemical studies (e.g., Livingston and Hutchinson, 1995). Recent surveys in Italy and Romania were also made by using a portable laser sensor, able to detect methane anomalies in the air (>2 ppmv) a few centimeters above the soil by hand-scanning a laser beam along tens of meters in the field. The instrument is a portable remote methane detector (Lasermethane™ SA3C06A, Tokyo Gas Engineering & Anritsu Corp.) based on infrared laser beam and wavelength modulation absorption spectroscopy (Iseki, 2004). The laser can scan a distance of 1 m to 150 m using retro-reflectors, expressing the methane column density in ppm × m, with a lower detection limit down to 1.3 ppm × m (depending on the operating conditions). This kind of measurement has allowed scanning wide areas in a short time (a 0.3 km^2 field can be scanned within 1 h), recognising the existence of microseepage in wide zones, with anomalies up to 40–50 ppmv of methane at 10–20 cm above the soil (Baciu et al., 2007).

3.1.1. Central Italy

A first regional-scale, reconnaissance survey has been performed along the Adriatic coast in central Italy, part of the Petroleum Basin codified as "Alps," n.4051 (USGS, 2000). This basin hosts conventional oil and gas plays; biogenic gas is exploited from sandy reservoirs down to 1100 m and thermogenic gas and oil occur in deeper carbonate reservoirs. Macro-seepage (including very small and often inactive mud volcanoes) is widespread throughout an area of about 6000 km^2. This area has been explored to detect methane anomalies in the air (Fig. 3): fifty small homogeneously distributed zones, about 10,000 m^2 in area, have been scanned during two surveys in 2005. In each zone, 3 parallel long-range (100 m) and 10 short-range (5–30 m) scans were performed. The average methane concentration in air was derived by dividing the column methane density (ppm × m) by the distances from sensor to the reflector, accurately measured by a laser distancemeter (Disto Lite 5, Leica Geosystems, Switzerland; accuracy: 2 mm). Site positioning was recorded by a GPS (Garmin eTrex Summit, US).

The data show that microseepage, defined as methane anomalies in the air within 20 cm above the soil, were detected in about 42% of the surveyed area (21 sites out 50; Figs. 3 and 4a). Microseepage, where flux was measured at 45 sites by closed chamber (as described in Section 4.1) actually does not occur throughout the TPS zone, but it is distributed in spotty areas. The spottiness and small-scale variation in flux was also described in Klusman (2003b, 2005, 2006). It appears that all of the microseeping areas fall within the boundary of

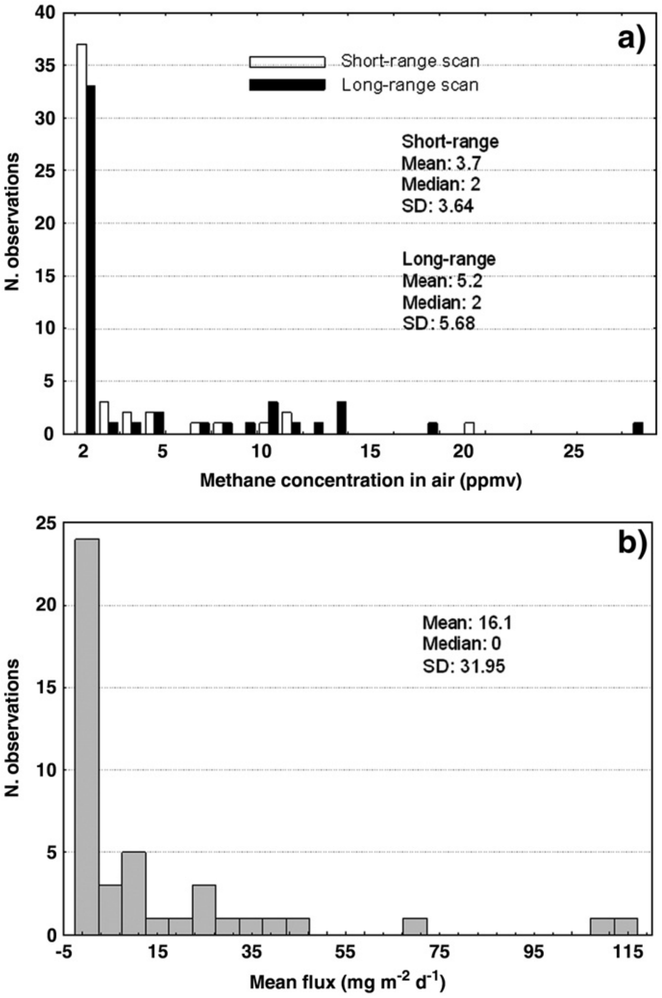

Fig. 4. Histogram of the distribution of (a) methane anomalies in air and (b) microseepage flux (mean values of 2 measurements in the same site) in the Adriatic-Central Italy hydrocarbon basin.

the gas/oil fields zone (sometimes corresponding to the area of minimum geographic extent of TPS; Magoon and Schmoker, 2000). Higher rates of microseepage occur above known hydrocarbon reservoirs (Fig. 3), e.g., the Cellino gas field, the S.Salvo Cupello gas field, and the newly discovered Miglianico oil field (placed in production in 2006); smaller microseepage rates occur elsewhere in the sedimentary basin.

3.1.2. Colorado and Wyoming (USA)

At the Rangely (Colorado) and Teapot Dome (Wyoming) oilfields, gas flux and soil gas surveys were carried out over areas of about 80 and 40 km^2, respectively (Fig. 5; Klusman, 2003a,b, 2005, 2006). During the course of these surveys, the atmospheric concentration of methane was determined at about 1 m above the soil. Fig. 6a–d shows the distribution of methane over the Rangely Field and a control area during winter and summer seasons (Klusman, 2003a). It could be argued that the higher methane concentrations observed over the field during the winter, relative to the control area were due to infrastructure leakage (Fig. 6a–b). However, during the summer measurements, the concentrations over the field and the control area were essentially the same (Fig. 6c–d). If infrastructure leakage were the cause, the field area would be higher in both seasons. This suggests that during the summer months, higher rates of methanotrophic oxidation in soils were able to consume the microseepage, while during the winter, methanotrophic oxidation slowed, and difference in methane concentrations between the field area and control area appeared.

In a further experiment to detect hydrocarbon seepage, 10-m deep holes were drilled at selected locations including areas with and without microseepage. The parameters used to make these selections were described in Klusman (2005). The 10-m deep holes were equipped to allow gas sampling at depths of 10, 5, 3, 2 and 1 m, allowing profiles of gas concentration to be measured. Fig. 7a, b shows the distribution of methane and propane in five 10-m holes drilled at Teapot Dome. The presence of propane, and the methane to propane ratio, provide strong evidence that the hydrocarbons were derived from thermogenic processes at depth (Whiticar, 1999). Three of the 10-m holes were drilled in anomalous areas (17, 18, 06), and two were on the field, but in areas where microseepage was not detected (02, 19). The hydrocarbon gradients in 10-m Hole 06 were substantially less than found in 17 and 18.

Partial oxidation of microseeping methane was occurring in the unsaturated zone profiles, as indicated by the carbon dioxide in the anomalous 10-m holes (Fig. 8a; Klusman, 2006). If the carbon dioxide was derived from oxidation of microseeping methane, the carbon dioxide should be “ancient” as shown by radiocarbon determination. Fig. 8b shows the radiocarbon age of the carbon dioxide in the 10-m holes (Klusman, 2006). The 10-m holes without microseepage (02, 19) have more modern carbon, reflecting oxidation of plant materials, refractory humic substances, and the very slow oxidation of the Cretaceous-age shale near the surface. The CO$_2$ carbon-14 measurement confirms that the microseepage is occurring at the present time. Carbon-14 ages approaching 40,000 years indicate continuous gas flow, not allowing mixing of “modern” atmospheric carbon dioxide by

Fig. 5. USA basins and oil fields where CH$_4$ flux measurements were made.
Modified from Klusman et al., 2000a; with permission from American Geophysical Union.

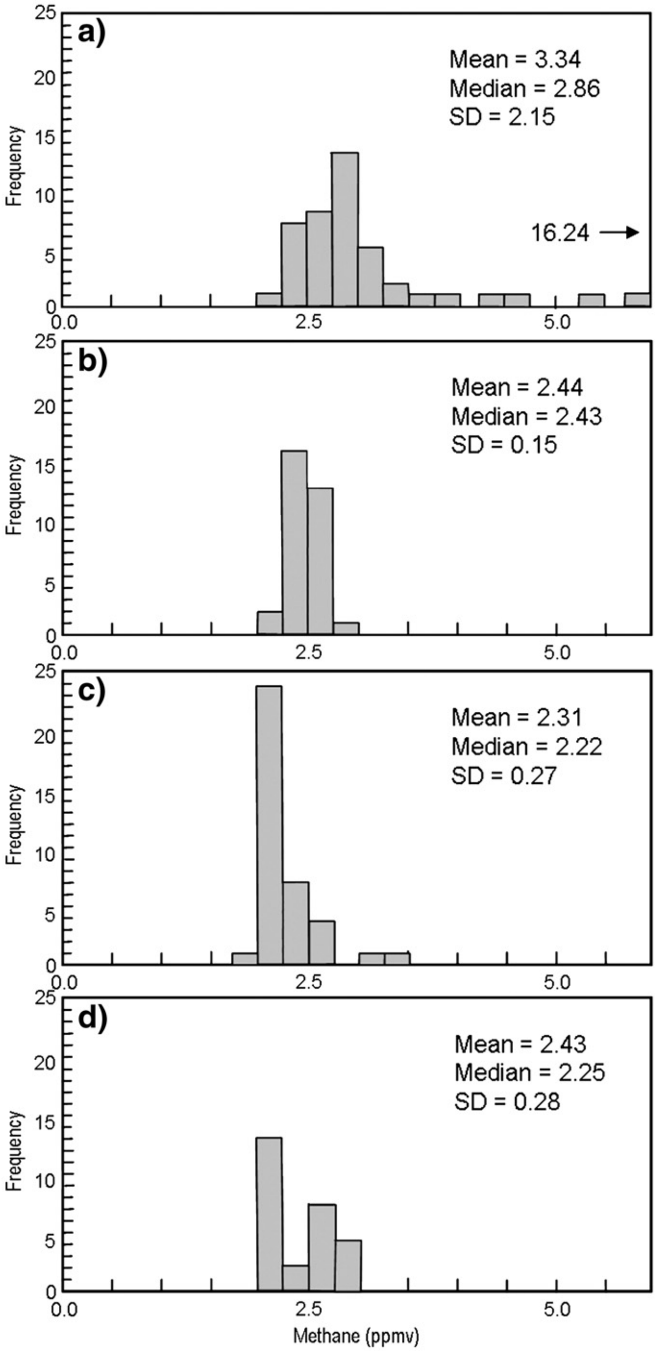

Fig. 6. Atmospheric methane measurements: (a) Rangely Field during the winter 2001/2002, (b) control area and Mellen Hill Fault during the winter, 2001/2002, (c) Rangely Field during the summer, 2001, and (d) control area and Mellen Hill Fault during the summer, 2001.
Modified from Klusman, 2003a, with permission from Elsevier.

barometric pumping. Stable carbon isotopic ratios of the methane and carbon dioxide in the 10-m holes also support the existence of active microseepage. Stable carbon isotopic ratios determined on calcium carbonate in cuttings from the 10-m holes indicate the microseepage has been occurring for a long time.

3.2. A new estimate of the extent of global microseepage

We can now assume, with more confidence relative to the previous estimates (Klusman et al., 1998; Etiope, 2005), that microseepage (actual positive flux of methane into the atmosphere) likely occurs within the area including oil/gas fields, and to a lesser extent, large areas of sedimentary basins.

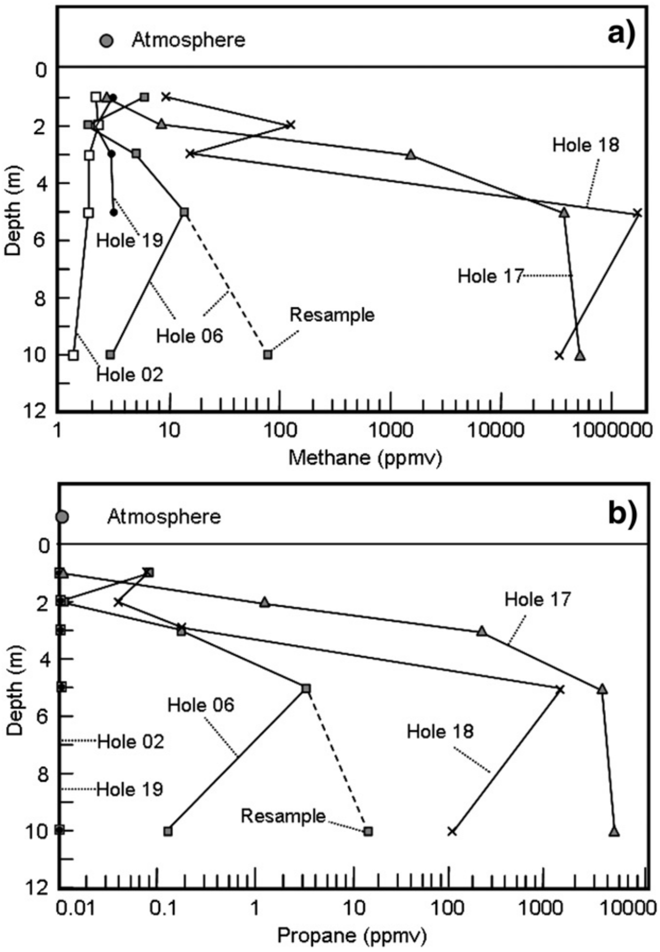

Fig. 7. a) Methane profiles in 10-m holes. b) Propane profiles in 10-m holes.

This area of possible microseepage can be assessed by accurate analysis of the distribution of oil/gas fields within all the 937 petroleum provinces or basins, reported in the GIS data-set of the U.S. Geological Survey World Petroleum Assessment 2000 and related maps (USGS, 2000). For each province a polygon has been drawn enclosing the gas/oil field points in the interactive maps (USGS, 2000), and the area has been estimated by graphic software. The extent of the oil/gas fields or plays (confirmed conventional plays) of the 72 United States petroleum provinces was determined by the respective "Geologic reports" and maps of the National Oil-Gas Assessment project (USGS, 1995). It appears that significant gas/oil field zones occur in at least 120 provinces. The total area of the gas/oil field zones is estimated to be between 3.5 and 4.2 million km^2, which is about 7% of global dryland area. This figure would be closer to the actual global microseepage area.

4. How large is the global microseepage emission into the atmosphere?

Preliminary models suggested that the hydrocarbon-prone sedimentary basins in a dry climate may produce a mean microseepage flux of 4.42 mg CH_4 m^{-2} day^{-1} (Klusman et al., 1998, 2000a); assuming 90% methanotrophic consumption at this microseepage rate in dry soil could lead to a global emission of methane of at least 7 Tg year^{-1}.

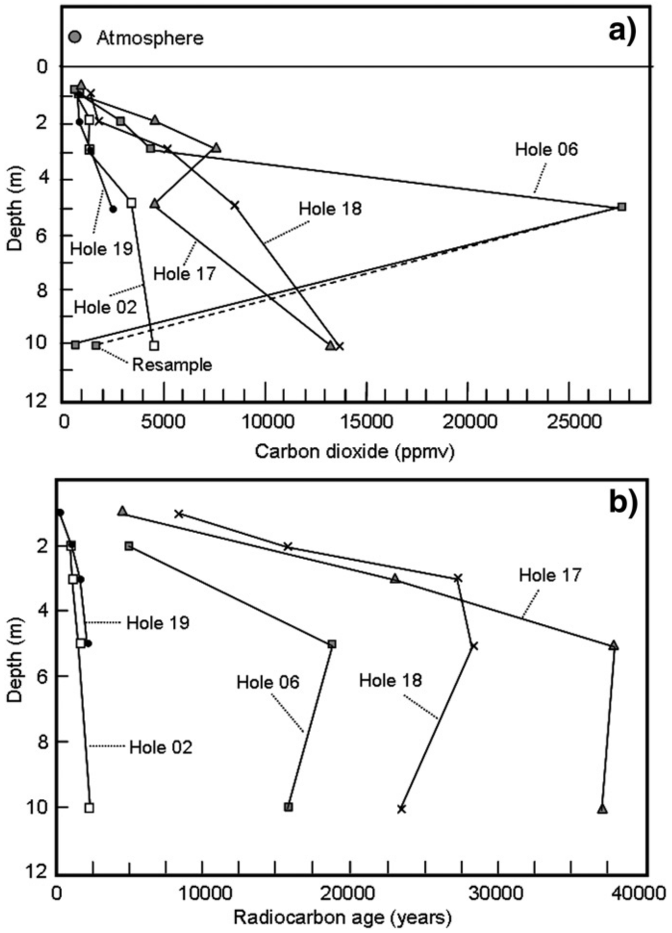

Fig. 8. a) Carbon dioxide profiles in 10-m holes. b) Radiocarbon age profiles of carbon dioxide in 10-m holes.

Global “potential” microseepage has been projected to 14–28 Tg year^{-1} (Etiope, 2005) on the basis of the global TPS area and a limited flux data-set. The surveys in progress are confirming that microseepage is in the range of some units or tens of mg m^{-2} day^{-1}, more rarely hundreds or thousands mg m^{-2} day^{-1} in smaller areas, corresponding with faults over the hydrocarbon reservoirs or around macro-seeps. Close to the macro-seeps (mud volcanoes or simple gas vents) the flux can reach 10^5 mg m^{-2} day^{-1} (Etiope et al., 2004a,b). Accordingly it is not possible to consider an average value for a given TPS. Homogeneously identifiable areas with different microseepage levels should be taken into account.

4.1. Microseepage flux in the onshore Adriatic TPS

In 2005 new flux data were acquired in hydrocarbon-prone sedimentary basins in Italy. Flux measurements were made by a closed chamber equipped with the laser detector described in Section 3.1 (Fig. 2c). The changing methane concentration inside the chamber was measured by the sensor for a short period of time. The flux is derived by knowing the rate of concentration increase and the chamber volume (42 liters) and geometry (Livingston and Hutchinson, 1995). For comparison, flux measurements were made also with a traditional 10 liter chamber (Etiope et al., 2004a,b) in 10 check points: flux values measured by the two chambers are coherent within 15%. Flux measurement reproducibility is within 10%. In total, 45 pairs of measurements were performed in 45 of the 50 sites monitored for atmospheric air (described in Section 3.1). At each site, two flux measurements were performed, spaced about 30–50 m apart; flux measurement density was thus in the order of 1 pair/20 km^2. In the fields having inactive gas seeps (small mud volcanoes), the measurements were performed at a distance not less than 50 m from the vent. Specific flux measurements on these macro-seeps have been carried out and are described elsewhere (Etiope et al., 2007b).

A positive flux of methane from the soil was measured, coherently, in the same fields where methane anomalies in the air were detected, plus in four other sites, where microseepage was too weak to produce detectable air anomalies. Nil or negative fluxes were measured in 58% of the sites investigated. The flux data suggest roughly two different levels of microseepage (Fig. 4b): lower microseepage, in the range 1–50 mg m^{-2} day^{-1} occurring in 81% of the microseepage fields (38% of total sites), and higher microseepage, from 50 to 190 mg m^{-2} day^{-1}occurring in 19% of the microseepage area (8% of total sites; generally in the oil–gas field zones; Fig. 3). Values above 190 mg m^{-2} day^{-1} were measured only in correspondence with macro-seeps within 10 m of the vents. This case-study suggests that for areas of the order of 10^3 km^2, hosting macro-seepage sites, at least two average flux values should be considered for upscaling, and extrapolation to larger areas.

4.2. Microseepage fluxes in the USA

Early methane microseepage flux measurements in hydrocarbon basins of Colorado, Wyoming, and Nevada were made in 1994-96 (Fig. 5 and Table 1). The methodology is described in Klusman et al. (2000a,b). Some locations measured in Denver-Julesburg, Piceance and Powder River basins specifically avoided known oil and gas fields; previous studies demonstrated however widespread methane anomalies in the soil over the entire Denver-Julesburg basin (e.g., Duchscherer and Mashburn, 1987). The locations in Railroad Valley were a mix of measurements over oil production and off the fields proper. More recently, the Rangely and Teapot Dome measurements were made on oil fields (Klusman, 2003a, 2005). The Rangely Field has both summer and winter flux and soil gas measurements, and is an over-pressured field. The Teapot Dome field is under-pressured, and the measurements were only made in the winter. Over-pressuring and under-pressuring are relative to hydrostatic pressure, and are critically important in the rate of vertical migration of buoyant fluids, as shown by the contrasting rates for Rangely vs. Teapot Dome (Table 1).

The modeled methane microseepage rates at Rangely, and from the highest producing formation at Teapot Dome were 59 and 0.74 mg m^{-2} day^{-1}, respectively. Ratioing the measured fluxes into the atmosphere from Table 1 to the modeled values gives the proportion passing into the atmosphere and not being oxidized by methanotrophs (0.3 for Rangely in winter, 0.1 for Rangely in summer, and 0.2 for Teapot Dome in winter).

4.3. Global microseepage

A further step in the estimate of global microseepage can now be made, assuming that microseepage occurs primarily within the gas/oil field boundary. Fig. 9 shows the histogram of all microseepage flux data from USA (excluding Duchscherer, 1981) and Europe listed in Table 1 (563 data examined). Most of data are averages of 2 or 3 measurements in the same site with different chambers; surveys have been performed in different seasons (summer and winter). The histogram suggests that at least three main levels of microseepage could be considered:

- Level 1: high microseepage (>50 mg m^{-2} day^{-1});
- Level 2: medium microseepage (5–50 mg m^{-2} day^{-1});
- Level 3: low microseepage (0–5 mg m^{-2} day^{-1}).

Levels 1 and 2 occur mainly in sectors hosting macro-seepage sites, and in the sedimentary basins in general, during winter. Of over 563 measurements, 276 are positive fluxes (49%); 3% are in the level 1

Table 1
Review of microseepage flux in hydrocarbon-prone areas. Microseepage in active mud volcano zones or close to macro-seeps (orders of 10^3–10^5 mg m^{-2} d^{-1}) is not considered.

	Reference	N. of sites	Area investigated (km^2)	Flux range (mean) (mg m^{-2} d^{-1})
United States				
Denver-Julesburg basin (Colorado)	Klusman et al. (2000a)	84	70,250	−41 to 43.1 (0.57)
Piceance (Colorado)	Klusman et al. (2000a)	60	12,130	−6.0 to 3.1 (−1.1)
Powder River (Wyoming)	Klusman et al. (2000a)	78	62,820	−14.9 to 19.1 (0.02)
Railroad Valley (Nevada)	Klusman et al. (2000a)	120	3370	−6.1 to 4.8 (−0.2)
Rangely (Colorado) winter	Klusman (2003a,b)	59	78	−8.60 to 865 (17.8)
Rangely (Colorado) summer	Klusman (2003a,b)	59	78	−4.02 to 145 (3.59)
Teapot Dome (Wyoming) winter	Klusman (2005; 2006)	39	42	−0.48 to 1.14 (0.14)
Music Mt. (Pennsylvania)	Duchscherer (1981)	na	na	100–200
Russia–Georgia–Azerbaijan				
Great Caucasus	Balakin et al. (1981)	na	na	430
Lesser Caucasus	Balakin et al. (1981)	na	na	12
Kura depression	Balakin et al. (1981)	na	na	8
Azerbaijan	Voitov (1975)	na	na	28 to 200
Romania				
Transylvania, Tarnaveni-Bazna	Etiope (2005)	5	5	2 to 64 (24)
Greece				
Western Peloponnesus				
Killini	Etiope et al. (2006)	19	0.04	−5 to 2520
Katakolo	Etiope et al. (2006)	9	0.25	44 to 7100
Italy				
Calabria				
S. Vincenzo la Costa	Etiope and Klusman (2002)	9	0.0003	−3 to 600 (174)
Abruzzo–Marche Adriatic coast				
Vasto	Etiope (2005)	30	2	−5 to 142 (22)
Pescara	Etiope (2005)	5	1	−4 to 13 (3.5)
Regional survey (6000 km^2)	This work	45	6000	−3 to 190 (16.1)
China				
Talimu Basin, Yakela Oil–Gas Field				
Oil–gas interface Sector	Tang et al. (2008)	5	50 m^2	2.4 to 3.5 (2.9)
Luntai Fault	Tang et al. (2007)	16	800 m profile	4.4 to 11 (7.6)

na: not available. Note: Each of the sites in Klusman et al., (2000a, b), Klusman (2003a;b), and Klusman (2005; 2006) consisted of triplicate measurements with 170-liter chambers set 10 meters apart (Fig. 2a). All of the basin studies and the Rangely Field consisted of repeated measurements at the same sites, in different seasons. The Teapot Dome field only had one survey in the winter of 2004. Measurements in Europe were carried out by 10-liter chambers in spring and summer seasons (Fig. 2b). The regional survey in Central Italy was performed by a 42-liter chamber equipped with laser sensor (Fig. 2c).

range (mean of 210 mg m^{-2} day^{-1}); level 2 represents about 12% of the surveyed areas (mean of 14.5 mg m^{-2} day^{-1}); level 3 is common in winter, far from macro-seepage zones, accounting for about 34% of the sedimentary zones surveyed (mean of 1.4 mg m^{-2} day^{-1}). Upscaling to the global microseepage area could be based on considering the average flux from each of the three microseepage levels and assuming that the percentage of occurrence of the different levels (3%, 12% and 34%) is valid at the global scale; this assumption does not give large errors because the result is not particularly sensitive to changing the percentages for several units. Also, measurements have been made in all seasons, so seasonal variations are incorporated in the 563 measurements. Accordingly, upscaling to all gas/oil field areas (see Table 2) would give a total microseepage in the order of 11–13 Tg $year^{-1}$; extrapolating to the global potential microseepage area (~8 million km^2) would project to an emission on the order of 25 Tg $year^{-1}$. These estimates are not far from the previous one (Etiope, 2005), and are coherent with the lower limit of 7 Tg $year^{-1}$ initially suggested by Klusman et al. (1998) and Etiope and Klusman (2002). However more measurements. in various areas and in different seasons, are needed to refine the 3-level classification and the actual area of seepage.

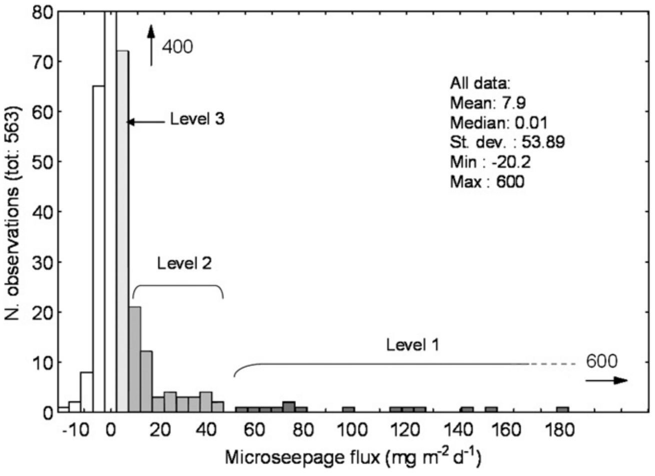

Fig. 9. Histogram of all microseepage flux data from USA and Europe. Three main levels of flux can be distinguished: level 1>50 mg m^{-2} day^{-1}; level 2 between 5 and 50 mg m^{-2} day^{-1}; level 3 between 0 and 5 mg m^{-2} day^{-1} (see Section 4.3). Data from Klusman et al., 2000a,b; Etiope and Klusman, 2002; Klusman, 2003a,b; Klusman, 2005, 2006; Etiope, 2005; Etiope et al. 2006, and this work.

5. What are the implications on global greenhouse gas budget?

If global microseepage is actually >10 Tg $year^{-1}$ it cannot be neglected in the atmospheric source/sink methane budget. Indeed microseepage is only one component of a wider range of geological

Table 2
Data used for the global microseepage emission estimate.

Microseepage level	Occurrence (%)	Average flux (t km^{-2} $year^{-1}$)	Oil/gas field area[a] (km^2)	Emission (Tg $year^{-1}$)
Level 1	3	76.7	105,000–126,000	8.4–9.8
Level 2	12	5.3	420,000–504,000	2–2.5
Level 3	34	0.5	1,190,000–1,428,000	0.6–0.7
Total	49			11–13

[a] The global oil/gas field area is estimated between 3.5 and 4.2×10^6 km^2, and it is assumed that microseepage occurs in 49% of this area (see text). Extrapolation to the total potential microseepage area (8×10^6 km^2) gives 24.8 Tg $year^{-1}$.

sources, which also include mud volcanoes, onshore and marine seeps and geothermal seepage (Etiope and Klusman 2002; Kvenvolden and Rogers, 2005). Including the microseepage emission estimated in this work, all geological sources would produce from 42 to 64 Tg CH_4 year^{-1} (Etiope et al., 2008a). The entire geological source would represent the second largest natural source of methane, after wetlands; it also represents almost 10% of the total emission of methane into the atmosphere. And 20–27% of the total natural sources considered by top-down and bottom-up models (IPCC, 2001; Etiope, 2004).

Microseepage, however, has its specific role in the global methane budget. Intrinsically, it suggests that not all drylands are a methane sink; basically the drylands which are part of petroleum basins and sedimentary basins having undergone thermogenesis, may not show methane uptake but positive exhalation into the atmosphere. If so, the global estimate of soil uptake should be re-assessed by removing from the up-scaling procedures for about 7 to 15% of global drylands areas.

The consensus value, 30 Tg year^{-1}, used also by the third IPCC Assessment Report (IPCC, 2001) could be overestimated. The large uncertainties in the global uptake (5 to 58 Tg year^{-1}) suggest that further efforts should be made to improve the estimate; the present work suggests that such efforts should include microseepage measurements in petroliferous basins.

6. Conclusions

A significant portion of drylands occur over sedimentary basins hosting natural gas and oil reservoirs, where gas migration to the surface (microseepage) takes place, producing positive fluxes of methane into the atmosphere, ranging from a few units to hundreds of mg m^{-2}d^{-1}. These fluxes have been determined at increasing numbers of locations, based on an understanding of the microseepage process, and where it can be expected to occur. Methanotrophic oxidation of methane in soils has been recognized, and its influence on the attenuation of microseepage determined.

Based on a relatively large and geographically dispersed data-set (563 measurements) from different hydrocarbon-prone sedimentary basins, it has been possible to improve the global estimates of microseepage extent and emission rates into the atmosphere. The global emission should be in the range 10–25 Tg year^{-1}, which is comparable to some estimates of the global methane sink in drylands (Potter et al., 1996). Microseepage, however, has never been mentioned as a natural methane source both in the "conventional" scientific literature and in the IPCC greenhouse gas emission inventories.

The data reported in the present work have strengthened, once again, the concept that microseepage of light hydrocarbon gases, specifically methane, cannot be ignored in the global atmospheric methane budget. In order to reduce the uncertainty of the global microseepage emission, it is necessary, however, to enlarge the flux data-set, including petroleum systems of different sedimentary basins.

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