Mud volcanoes and microseepage: the forgotten geophysical components of atmospheric methane budget

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Abstract
Mud volcanoes and microseepage are two important natural sources of atmospheric methane, controlled by neotectonics and seismicity. Petroleum and gas reservoirs are the deep sources, and faults and fractured rocks serve as main pathways of degassing to the atmosphere. Violent gas emissions or eruptions are generally related to seismic activity. The global emission of methane from onshore mud volcanoes has recently been improved thanks to new experimental data sets acquired in Europe and Azerbaijan. The global estimate of microseepage can be now improved on the basis of new flux data and a more precise assessment of the global area in which microseepage may occur. Despite the uncertainty of the various source strengths, the global geological methane flux is clearly comparable to or higher than other sources or sinks considered in the tables of the Intergovernmental Panel on Climate Change.

Key words *methane – lithosphere degassing – mud volcanoes – greenhouse gas – geodynamics*

1. Introduction

Geodynamics and geophysical processes of lithosphere degassing are generally neglected in contemporary global climate change research. Nevertheless, recent studies have suggested that lithosphere carbon dioxide (CO_2) and methane (CH_4) outgassing is an important component of the natural greenhouse gas sources (Etiope and Klusman, 2002; Morner and Etiope, 2002). This is particularly evident for methane, whose geological sources have been object of detailed investigations during recent years. Methane is one of the main greenhouse gases playing a significant role in global climate changes, on geological, Quaternary and contemporary time scales. Natural sources of methane include wetlands (> 100 Mt yr^{-1}), termites (20 Mt yr^{-1}) and oceans (10 Mt yr^{-1}). The Intergovernmental Panel on Climate Change (IPCC, 2001) does not include in its official tables any geological source of methane, apart from hydrates (5-10 Mt yr^{-1}). Only recently, it has been suggested that several geologic processes may lead to the release of significant amounts of methane into the atmosphere, mainly from submarine seepage, mud volcanoes and microseepage (Etiope and Klusman, 2002; Etiope *et al.*, 2003, 2004a; Milkov *et al.*, 2003; Etiope and Milkov, 2004).

Today's global estimates available for methane flux from these sources are probably underestimated and have a great potential of being increased. This work aims at evaluating this potential for mud volcanoes and microseepage, discussing present limits and introducing new data. The global microseepage estimate is re-calculated on the basis of an upgraded experimental data set and on a new evaluation of the global microseepage area.

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2. Mud volcano emissions

Mud Volcanoes (MVs) are the largest surface expression of migration of hydrocarbon fluids through neotectonic faults in petroleum-bearing sedimentary basins (fig. 1). Geology and formation mechanisms are described in a wide literature (*e.g.*, Milkov, 2000; Dimitrov, 2002; Revil, 2002). Methane flux from MVs is object of detailed studies only starting from 2001, when the main terrestrial MVs of Europe, located in Romania and Italy were investigated (Etiope *et al.*, 2002, 2003, 2004a). More recently, gas flux has been measured in Azerbaijan, which hosts the world's biggest MVs and densest MV population (Etiope *et al.*, 2004b).

Thanks to these studies, it has been possible to elaborate a first estimate of global emission of methane from MVs to the atmosphere, that is at least 6-9 Mt yr^{-1} (Etiope and Milkov, 2004). This is the same level of the estimates today considered for ocean and hydrates sources.

Methane emission from MVs (fig. 2) includes not only the gas flux from localised vents (craters, gryphons, bubbling pools and salses) but also the diffuse exhalation from soil, known as microseepage, whose mechanisms are discussed in the next section. The data collected from 2001 to 2003 in Europe and Azerbaijan (Etiope *et al.*, 2002, 2003, 2004a,b) refer to the quiescent degassing. It is known however that many MVs, especially those in Azerbaijan, can erupt violently, generally in relation to seismic activity, injecting huge amounts of gas into the atmosphere within a few hours. So far, however, only some rough estimates of the eruptive flux of MVs in Azerbaijan have been reported, generally based on subjective visual observations. For example, it has been reported that during the eruption of the Touragai mud volcano (Azerbaijan) in 1946, about 0.36 Mt of CH_4 were emitted, and more than 40 000 t of CH_4 emitted from the Duvannyi Island volcano in 1961. Bolshoi Maraza erupted for three days in 1902 injecting more than 80 000 t of CH_4 into the atmosphere (Guliyev and Feyzullayev, 1997). From 1810 until the present, about 250 eruptions of 60 mud volcanoes have been observed in Azerbaijan. Sokolov *et al.* (1969) described violent eruptions of mud-volcanoes in the southern Caspian Basin, which have released hundreds of millions of cubic meters of gas and estimated that mud volcanoes in Azerbaijan have produced 10^6 Mt of gas in the last million years. Most of these eruptions followed large earthquakes. In their global estimation of gas flux from mud volcanoes, Milkov *et al.* (2003) concluded that the global eruptive degassing may be approximately equal to the global quiescent degassing. In contrast, Dimitrov (2002) suggests that gas flux from quiescent periods is significantly (by a factor of up to 30) less than the gas flux during eruptions.

Direct measurements of methane flux from submarine MVs have rarely been performed (Linke *et al.*, 2005), and only in a few active points. Some rough estimates, generally based on the volumes of mud extruded, are available as reviewed by Kopf (2002). On the basis of available data, including MVs dimensions, depth and gas dissolution models, Etiope and Milkov (2004) have estimated that at least 0.5 Mt of methane are injected into the atmosphere from MVs occurring at depths less than 200 m (shelf MVs). However, recent discoveries (*e.g.*, Holland *et al.*, 2003) suggest that shelf MVs are

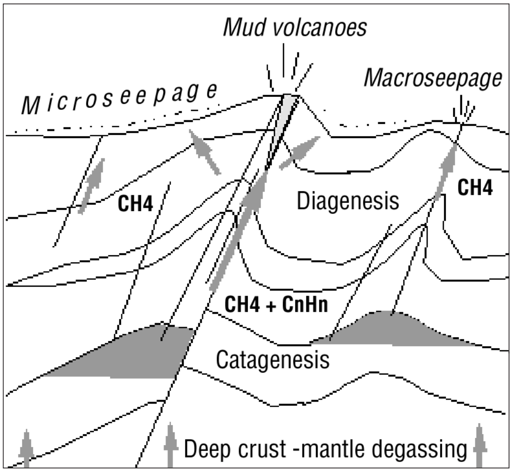

Fig. 1. Sketch of methane origin and emission in hydrocarbon-prone basins.

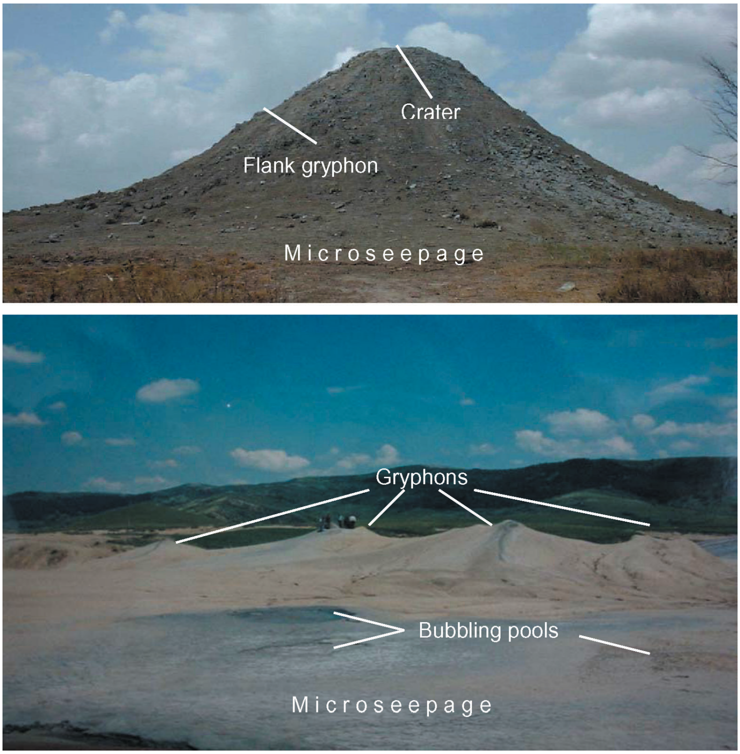

Fig. 2. Typical mud volcano morphology and methane emission structures: (*top*) single crater MV, Trinidad (from the Geological Society of Trinidad and Tobago); (*bottom*) multi-crater (gryphons) MV, Paclele (Eastern Romania).

more abundant than previously assumed and that many of them release significant amounts of gas bubble plumes, which may easily cross the water column and enter the atmosphere.

Therefore detailed studies and measurements of gas flux during eruption, and direct measurements of gas flux from submarine mud volcanoes appear to be critical to further constrain the global gas flux from MVs.

3. Microseepage

Etiope and Klusman (2002) defined microseepage as 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. 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; Klusman and Saeed, 1996; Matthews, 1996); 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 along faults, especially those produced by neotectonics (Klusman, 1993; Etiope, 1999).

In dry lands, methane flux is generally negative, from the atmosphere to the soil, due to methanotrophic oxidation by CH_4-consuming bacteria in the soil. Due to this biological activity, dry lands are considered a net sink of atmospheric methane, on global scale (around 30 Mt yr^{-1}), with fluxes generally in the order of –5 to –1 mgm^{-2}d^{-1} (Dong *et al.*, 1998). Microseepage is instead responsible for less negative or positive fluxes of methane, indicating that soil consumption can be lower than the input from underground sources. The positive fluxes are typically of a few units or tens of mgm^{-2}d^{-1}, but may be at the hundreds level over wide tectonised and faulted areas in the most active microseeping regions. These values are comparable with the CH_4 emission in wet, anaerobic ecosystems, which are typically in the range 1-500 mgm^{-2}d^{-1} (Batjes and Bridges, 1994). In MV areas microseepage may easily reach fluxes in the order of 10^3-10^5 mgm^{-2}d^{-1}. The highest microseepage flux ever reported has been found close to the fire of Yanardag, in Azerbaijan: > 560 000 mgm^{-2}d^{-1} (Etiope *et al.*, 2004b). A review is made by Etiope and Klusman (2002), and data on microseepage linked to MVs are in Etiope *et al.* (2002, 2003, 2004a,b).

The global coverage of microseepage is unknown. Potentially, microseeping areas are all the sedimentary basins in a dry climate, with petroleum and gas generation processes at depth: this area has been estimated to be around 43 366 000 km^2 (Klusman *et al.*, 1998). Preliminary models suggest that this area can produce a mean microseepage flux of 4.42 mg CH_4 m^{-2}d^{-1} (Klusman *et al.*, 1998, 2000) and 90% of methanotrophic consumption leading to a global emission of methane of about 7 Mt yr^{-1}. This is only a first, rough estimate, very likely quite conservative.

Today it is possible to suggest another estimate, based directly on experimental values and on the area of the tectonic zones (faulted) actually hosting gas reservoirs. We have first to distinguish microseepage close to MVs (MV microseepage) and microseepage far from MVs or in sedimentary basins without MVs (simply microseepage). Global emission of MV microseepage has already been estimated by Etiope and Milkov (2004), who considered the diffuse flux occurring within the MV morphologic structure (hill, muddy cover, and external bound of 250 m); this MV microseepage is at least 1-2.4 Mt yr^{-1}.

3.1. *Upgraded microseepage data-set*

In order to estimate the global non-MV microseepage it is possible to refer to an upgraded data-set, including microseepage from United States (Klusman *et al.*, 2000), former Soviet Union (Voitov, 1975; Balakin *et al.*, 1981) and new data from reconnaissance surveys, carried out in 2002, in non-MV zones of Transylvania, central Romania and along the Adriatic coast of central Italy. These are two of the most important gas producing areas of Europe (Schlumberger, 1987; Cranganu and Deming, 1996). In these areas, 40 soil-atmosphere flux measurements were carried out in soils hosting wheat and grass communities, typical of temperate climates, by closed-chamber method; gas was analysed in duplicate by portable micro-GC (Etiope *et al.*, 2002).

The flux values ranged from –5 to 142 mgm^{-2}d^{-1}, with a mean of 20 mgm^{-2}d^{-1}. Only 6 flux values were negative (from –5 to –1.5 mgm^{-2}d^{-1}); the highest values (from 90 to 142 mgm^{-2}d^{-1}) were measured in the «Cupello» gas reservoir (Vasto) on the Italian Adriatic coast. Here biogenic gas is exploited from sandy reservoirs at depths between 800 and 1100 m and thermogenic gas occurs in deeper carbonate reservoirs (Schlumberger, 1987). The average microseepage value derived from the surveys cited in table I (excluding the higher values of Great Caucasus and Azerbaijan) is around 10 mgm^{-2}d^{-1}.

3.2. *New estimate of global microseepage area*

The flux data available today suggest that microseepage corresponds closely to the spatial distribution of underground petroleum reservoirs. Instead of considering the whole area covered by sedimentary basins, as made by Klusman *et al.* (2000), it is today possible to estimate the global area of the onshore petroleum reservoirs. This has been made elaborating the data from the last US Geological Survey World Petroleum Assessment (USGS, 2000). This work named and mapped 159 of the largest total petroleum systems (TPS's) in the world using geographic information system. The TPS's are the hydrocarbon-fluid systems in the lithosphere including the essential elements and processes

Table I. Microseepage in hydrocarbon-prone (no mud volcanos) areas.

	Reference	No. of sites	Flux range (mean) $mgm^{-2}d^{-1}$
Denver-Julesburg Basin (Colorado)	Klusman *et al.* (2000)	84	– 41 to 43.1 (0.57)
Piceance (Colorado)	Klusman *et al.* (2000)	60	– 6.0 to 3.1 (– 1.1)
Powder River (Wyoming)	Klusman *et al.* (2000)	78	– 14.9 to 19.1 (0.02)
Railroad Valley (Nevada)	Klusman *et al.* (2000)	120	– 6.1 to 4.8 (– 0.2)
Great Caucasus	Balakin *et al.* (1981)	Unknown	430
Lesser Caucasus	Balakin *et al.* (1981)	Unknown	12
Kura depression	Balakin *et al.* (1981)	Unknown	8
Azerbaijan	Voitov (1975)	Unknown	28-200
Transylvania (Central Romania)			
Tarnaveni-Bazna	This work	5	2 to 64 (24)
Abruzzo Adriatic coast (Central Italy)			
Vasto	This work	30	– 5 to 142 (22)
Pescara	This work	5	– 4 to 13 (3.5)

needed for oil and gas accumulations, migration and seeps. It is assumed, therefore, that microseepage occurs throughout the onshore TPS areas. Based on a careful analysis of TPS map and GIS data-sets, the global microseepage area can be estimated in the order of 8×10^6 km^2.

Assuming conservatively a mean microseepage in the range 5-10 $mgm^{-2}d^{-1}$, a simple scaling-up would give a global emission of 14-28 Mt yr^{-1}.

4. Conclusions

Mud volcanoes and microseepage are closely related to neotectonic and seismic processes, and represent two important natural sources of atmospheric methane. The estimate of global emission of methane from onshore mud volcanoes has recently been refined thanks to new experimental data sets acquired in Europe and Azerbaijan. Global microseepage has been estimated with less accuracy due to the few measurements available. A refinement is here proposed considering new data from hydrocarbon areas in U.S.A., former Soviet Union, Romania, Italy, and a more accurate assessment of the global area in which microseepage may occur. Potentially, the resulting global microseepage output can be in order of 14-28 MT yr^{-1}. This is a provisional estimate based on the assumption «microseepage area = TPS area». A large number of data over wide areas, from different TPS, and more accurate scaling-up procedures are necessary to reach a more constrained estimate.

Given these uncertainties, the global emission of methane from geological sources, including MVs (6-9 Mt yr^{-1}), marine seepage (20 Mt yr^{-1}), geothermal flux (2.5-6.3 Mt yr^{-1}) and microseepage in petroliferous basins (14-28 Mt yr^{-1}) would amount at least to 40-60 Mt yr^{-1}. The previous estimate was 35-45 Mt yr^{-1} (Etiope and Milkov, 2004). These numbers are of the same level of or higher than other sources or sinks considered in the tables of the Intergovernmental Panel on Climate Change (IPCC, 2001), such as biomass burning (40 Mt yr^{-1}), termites (20 Mt yr^{-1}), oceans (10 Mt yr^{-1}) and soil uptake (30 Mt yr^{-1}). These results show clearly that geologic methane sources, strictly controlled by geodynamic and tectonic processes, have a primary role in the atmospheric greenhouse gas budget.

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