Chapter 2
Gas Seepage Classification and Global Distribution

The surface expressions of natural gas seepage can be classified on the basis of spatial dimension, visibility, and fluid typology, as summarised in the following scheme:

$$\text{Macro-seeps}\begin{cases}\text{Focused flow} & \begin{cases}\text{Gas seeps}(\textit{gas only})\\ \text{Oil seeps } (\textit{gas and oil})\\ \text{Gas-bearing springs } (\textit{dissolved gas})\\ \text{Mud volcanoes } (\textit{gas, water and sediments})\end{cases}\\ \text{Diffuse flow} & \text{Miniseepage (invisible)}\end{cases}$$

$$\text{Microseepage}\{\text{Diffuse flow} \quad \text{(invisible, independent from macro-seeps)}$$

Macro-seeps (or seeps) are "channelled" flows of gas, typically related to fault systems. Gas flux is expressed in terms of mass/time (e.g., kg/day or tons/year). Microseepage is the pervasive, widespread exhalation of gas throughout relatively large areas, conceptually independent from seeps, even if also enhanced along faults. Gas flux is expressed in terms of mass/area/time (for methane it is usually in mg m^{-2} day^{-1}). Sometimes the term "micro-seeps" is used in the scientific literature, especially in the marine environment (e.g., Hovland et al. 2012) to define relatively smaller seeps, not observable, for example, by hydroacoustic methods. However, the term can be misleading as it may be confused with microseepage. The classification in the above scheme is, in theory, valid for either subaerial (land-based) or underwater (marine and lake) environments. As discussed in Sect. 2.3, the marine environment can have specific gas-seepage structures.

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2.1 Macro-Seeps

2.1.1 Gas Seeps

Gas seeps are fluid manifestations that release only a gaseous phase (Figs. 2.1 and 2.2). They can also be called "dry seeps". Gas may vent from outcropping rocks, through the soil horizon, or through river/lake beds. Since surface water is only crossed by gas flow, gas bubbling from groundwater filled wells, or other shallow water bodies, should be considered dry seeps. Gas seeps may also manifest with strong odours, an absence of vegetation, wet bubbly ground, abnormal snow-melt patterns, and may lead to soil temperature anomalies. As discussed in greater detail in Sect. 5.3, the origin of the gas is mainly thermogenic (and abiotic in special cases, see Chap. 7), and subordinately microbial and mixed.

Methane-rich gas flowing through rocks and dry soil can self-ignite and produce so-called "eternal fires", the presence of a continuous flame as reported in historical records. However, any dry gas seep with a sufficiently focused and intense CH_4-rich gas flow can burn by artificial ignition, for example, with a lighter. "Eternal flames", such as those of Yanardag in Azarbaijan, Baba Gurgur in Iraq, or Chimaera in Turkey (Fig. 2.2), have particular charm and as discussed in Chap. 9 are frequently associated with ancient religious traditions and myths.

Methane fluxes, either from individual vents or from an entire macro-seepage area (including miniseepage), may span a wide range of values, on the order of 10^{-1}–10^{3} tonnes/year. Table 2.1 presents methane fluxes directly measured in the field from gas seeps (and oil seeps, springs, and mud volcanoes, as described below). Methane flux from large seep fires, such as Yanardag or Baba Gurgur, may exceed 10^{3} tonnes/year (the Yanardag flux provided in Table 2.1 refers only to a small portion of the miniseepage surrounding the large flames; see Fig. 2.2). For gas vents with a diameter <1 m, the flux is typically between 0.1 and 100 tonnes/year.

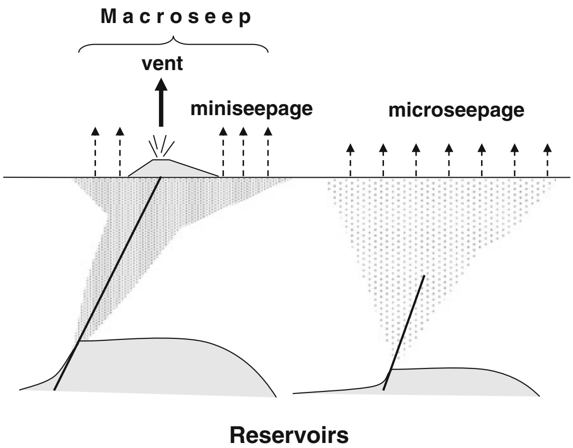

Fig. 2.1 Conceptual sketch of macro-seeps, miniseepage, and microseepage

Fig. 2.2 Examples of gas seeps and “eternal fires”. **a** Deleni, Romania; **b** Yanardag, Azerbaijan; **c** Giswil, Switzerland; **d** Baba Gurgur, Iraq; **e** Chimaera, Turkey; and **f** Faros-Katakolo, Greece. (*Photo credits* **a**, **c**, **e**, and **f** G. Etiope; **b** L. Innocenzi; **d** http://www.en.wikipedia.org/wiki/File:P3110004.jpg)

The flux is generally constant over time and only weaker gas seeps, with fluxes below 1 tonnes/year, show variations in their activity in response to seasonal, meteorological, and additional factors (e.g., aquifer conditions).

A main characteristic of seep fires is that because the size of the flame is proportional to gas flow (F in g/s) according to the following equations (Delichatsios 1990;

Table 2.1 Methane flux from seeps, as measured by closed-chambers or the inverted funnel systems described in Chap. 4

Country	Type	Seep-site name	CH_4 flux (ton/year)	References
Azerbaijan	Gas	Yanardag (*miniseepage only*)	>68	Etiope et al. (2004)
	MV	Lokbatan	342	Etiope et al. (2004)
	MV	Kechaldag	94	Etiope et al. (2004)
	MV	Dashgil	843	Etiope et al. (2004)
	MV	Bakhar	45	Etiope et al. (2004)
Greece	Gas	Katakolo Faros	68	Etiope et al. (2013a)
	Gas	Katakolo Harbour	21	Etiope et al. (2013a)
	Gas	Killini	1.4	Etiope et al. (2006)
	Gas	Patras Coast	1.2	Etiope et al. (unpublished)
Italy	Gas	Montechino	100	Etiope et al. (2007)
	Gas	Miano	200	Etiope et al. (2007)
	Gas	M.Busca fire	9.2	Etiope et al. (2007)
	Gas	Censo fire	6.2	Etiope et al. (2007)
	Gas	Occhio Abisso	2.7	Etiope et al. (2007)
	MV	Rivalta	12	Etiope et al. (2007)
	MV	Regnano	34	Etiope et al. (2007)
	MV	Nirano	32.4	Etiope et al. (2007)
	MV	Ospitaletto	1.4	Etiope et al. (2007)
	MV	Dragone	0.3	Etiope et al. (2007)
	MV	Bergullo	1	Etiope et al. (2007)
	MV	Pineto	2.7	Etiope et al. (2007)
	MV	Astelina (Cellino Attanasio)	0.5	Etiope et al. (2007)
	MV	Frisa Lanciano	1.9	Etiope et al. (2007)
	MV	Serra de Conti	3.3	Etiope et al. (2007)
	MV	Offida	1.8	Etiope et al. (2007)
	MV	S.Vincenzo la Costa	0.02	Morner and Etiope (2002)
	MV	Puianello	0.12	Etiope (unpublished)
	MV	Rotella	0.1	Etiope (unpublished)
	MV	Vallone	0.05	Etiope (unpublished)
	MV	Maccalube Aragona	394	Etiope et al. (2002)
	MV	Paternò Stadio	2.1	Etiope et al. (2002)
	Oil	Madonna dell'Olio Bivona	0.02	Etiope et al. (2002)
	Spring	Tocco da Casauria	0.01	Etiope (unpublished)
Japan	MV	Murono Tokamachi	>20	Etiope et al. (2011b)
	MV	Kamou (Gamo) Tokamachi	3.7	Etiope et al. (2011b)

(continued)

Table 2.1 (continued)

Country	Type	Seep-site name	CH_4 flux (ton/year)	References
Romania	Gas	Andreiasu	50	Etiope et al. (2004)
	Gas	Bacau Gheraiesti	40	Baciu et al. (2008)
	Gas	Bazna	0.4	Spulber et al. (2010)
	Gas	Praid	4.4	Spulber et al. (2010)
	Gas	Deleni	~20	Spulber et al. (2010)
	Gas	Sarmasel	595	Spulber et al. (2010)
	MV	Fierbatori	37	Etiope et al. (2009)
	MV	Paclele Mari	730	Etiope et al. (2009)
	MV	Paclele Mici	383	Etiope et al. (2009)
	MV	Beciu	>260	Etiope et al. (2009)
	MV	Homorod	1	Spulber et al. (2010)
	MV	Monor	16	Spulber et al. (2010)
	MV	Valisoara	0.03	Spulber et al. (2010)
	MV	Filias	0.4	Spulber et al. (2010)
	MV	Porumbeni	0.5	Spulber et al. (2010)
	MV	Cobatesti	1.6	Spulber et al. (2010)
	MV	Boz	0.2	Spulber et al. (2010)
Switzerland	Gas	Lago Maggiore Ten	71	Greber et al. (1997)
	Gas	Giswil	>16	Etiope et al. (2010)
Taiwan	Gas	Suei-huo-tong-yuan	0.97	Yang et al. (2004)
	Gas	Chu-Ho	75.7	Hong et al. (2013)
	MV	Luo-shan	0.1	Yang et al. (2004)
	MV	Chunglun (CL#02)	1.43	Yang et al. (2004)
	MV	Kuan-tze-ling	0.08	Yang et al. (2004)
	MV	Yan-chao	0.7	Yang et al. (2004)
	MV	Gung-shuei-ping	1.1	Yang et al. (2004)
	MV	Diang-kuang	0.7	Yang et al. (2004)
	MV	Hsiao-kung-shuei	1	Hong et al. (2013)
	MV	Hsin-yang-nyu-hu	2.2	Hong et al. (2013)
	MV	Wu-shan-ding	35	Hong et al. (2013)
Ukraine	MV	Boulganack	40	Herbin et al. (2008)
USA California	Gas + Oil	Ojai Valley seeps	3.6	Duffy et al. (2007)
New York	Gas	Chestnut Ridge Park	0.3	Etiope et al. (2013b)
Colorado	Gas	Raton Basin seep Apogee 643	908	LTE (2007)
Colorado	Gas	Raton Basin seep Apogee 644	86	LTE (2007)

In most cases, the flux includes emissions from vents and from surrounding miniseepage (*Gas* gas seeps; *MV* mud volcanoes; *Oil* oil seeps)

Hosgormez et al. 2008; Etiope et al. 2011c), they provide visual information regarding the amount of gas released:

$$F = \frac{Q}{Hc} \tag{2.1}$$

$$Q = (\frac{Z_f}{0.052})^{3/2} * P \tag{2.2}$$

where Q is the heat release rate (kW or kJ/s), Hc is the heat of combustion (kJ/g), Z_f is the flame height, and P is the flame perimeter (P = 4D in m; D is estimated at the base of the flame). Theoretical results obtained using this correlation are fairly consistent with those of direct flux measurements obtained from several seep fires investigated in Turkey, Greece, Italy, Romania, and Switzerland (Etiope et al. 2006, 2007, 2010, 2011c). Significant uncertainties may be associated with visual estimates of Z_f and D, and additional factors may influence flame height (e.g., cross winds). The correlation used is, therefore, less valid for very large and turbulent flames (once the turbulent regime is reached, flame height does not change with increasing flow rate). For the worst conditions, however, the method provides an estimate for the order of magnitude of the gas emissions, attributing at least a range of possible fluxes to each flame. For example, a flame approximately 50 cm high with a diameter above 10 cm is typically related to a gas flux higher than 15 kg/day; a small flame of 10 × 5 cm is typical related to a flux below 5 kg/day.

2.1.2 Oil Seeps

Oil seepage is not the object of this book but it is considered here because oil is frequently accompanied by a gaseous phase, especially when oil and gas coexist within a reservoir. The amount of gas in oil seeps decreases during oil exposure to the atmosphere, with subsequent oxidation, biodegradation, and solidification. Asphalts and tars (solid seeps) do not generally contain significant quantities of gas. The gas associated with oil is typically thermogenic and particularly rich in alkanes heavier than methane, from ethane to butane, with a wetness, $\Sigma C_{2-5}/\Sigma C_{1-5}$ (see the notation in Chap. 1), generally higher than 5–10 %. As a result, oil seeps are special natural sources of atmospheric ethane and propane, which, as discussed in Chap. 6, are photochemical pollutants and ozone precursors. Oil seeps may form black oil-filled pools, or produce oil that flows from rocks or soils or oil-impregnated terrains where the oil flow is episodic. In aquatic environments, oil is visible as drops, surrounded by iridescences, slicks (layers of buoyant oil), oily patches, or as diffuse iridescences. Oil is also released from mud volcano structures (see below) and for these cases oil emission points are an integral part of the mud volcano seepage system. For inventory purposes, these oil manifestations should not be considered as independent seeps.

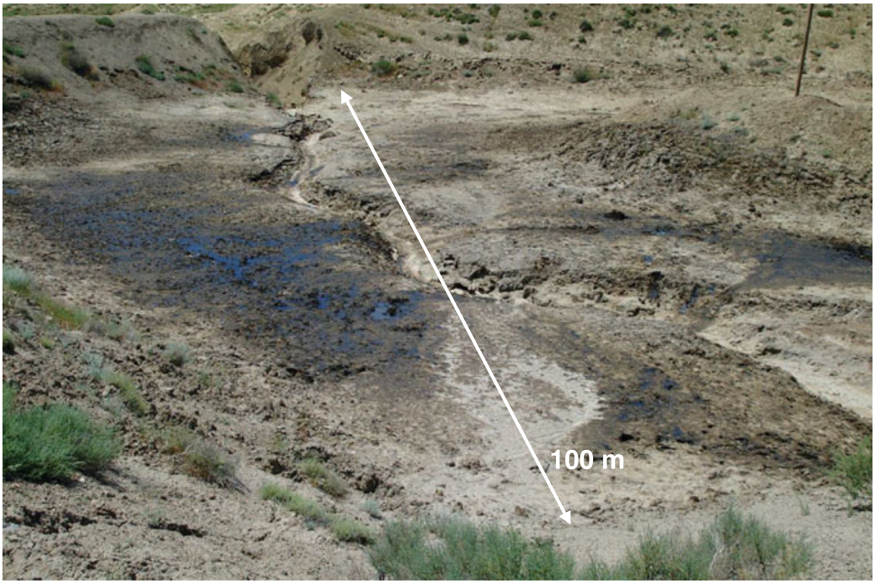

Fig. 2.3 The oil seep at Dashgil, Azerbaijan (*photo* by L. Innocenzi, INGV)

Geological evidence indicates that many historical oil seeps have disappeared today or that their fluid activity has been strongly reduced due to vigorous petroleum extraction that began in the 1800s (see Chap. 8). The decrease of oil flow is a result of the decrease of fluid pressures inside reservoirs. A large number of oil manifestations from the Alpine–Himalayan, Pacific Ocean, and Caribbean sedimentary belts, as described in the 20th century's petroleum geology literature (e.g., Link 1952), no longer exist. Nevertheless, almost all petroleum basins currently contain active oil seeps, numbering in the thousands. Some of the most active and large onshore oil seeps can currently be observed in Azerbaijan (near Dashgil, Fig. 2.3), Alaska (Samovar Hills), California (e.g., the McKittrick and Sargent oil fields), Pulkhana (Iraq), Kuwait (e.g., Burgan), and New Zealand (Kōtuku).

2.1.3 Gas-Bearing Springs

Freshwater springs and shallow aquifers may contain variable concentrations of dissolved methane originating from modern, microbial processes. As discussed in Chap. 1, this background methane should not be labelled seepage. In theory, this type of background methane should only occur when groundwater conditions are sufficiently reducing, with very low dissolved oxygen (DO) concentrations; otherwise the gas is rapidly oxidised limiting the presence of "non-seepage" methane in confined aquifers. In practice, microbial methane can be found in any type of aquifer (e.g., Darling and Gooddy 2006), with concentrations ranging from 0.05 μg/L (a typical lower detection limit) to mg/L levels. Unravelling this background methane and eventual seeping methane is only possible using analyses of the C and H isotopic composition of CH_4 and additional dissolved alkanes (ethane, propane, etc.).

For the case of seeping gas, groundwater from the springs of mineral waters and artesian aquifers may release an abundant gaseous phase to the atmosphere (Table 2.1, Fig. 2.4). Water may have a deep origin and may have interacted with gas during its ascent to the surface. Due to depressurization and water turbulence, degassing mainly occurs at the spring outlet. Mineral water springs have often been neglected as the vehicle of hydrocarbons from subsurface accumulations and few data (concentrations and/or degassing fluxes) for dissolved gases are available for petroleum-bearing sedimentary basins. Studies on the environmental impact of petroleum production, especially with reference to hydraulic fracking for shale-gas production within the United States, have recently provided new datasets indicating that groundwater containing natural methane (on the order of tens of mg/L) is more common than previously thought (e.g., Kappel and Nystrom 2012; Warner et al. 2013; also see Sect. 6.2). Due to possible links with subsurface petroleum accumulations, gas-bearing springs have also been the object of recent research in Europe, in particular in Italy and Romania (e.g., Ionescu 2015).

A useful example is that of the Tocco da Casauria spring, located in the Apennine Mountains of central Italy (Fig. 2.4). The spring is historically known for

Fig. 2.4 The gas and oil bearing spring of Tocco da Casauria, Central Italy (*photo* by G. Etiope)

episodic releases of oil, visible as iridescences in the water. The molecular composition and flux of the evolved gas from the water was measured on site using a portable spectrometer (a Fourier Transform Infrared, FTIR) linked to a closed-chamber (also see Chap. 4). The spring outlet was found to release more than 20 g of CH_4 per day, with a flux that gradually decreased along the water stream. Flowing water releases gas tens of meters from the spring. The soil surrounding the spring also exhales gas with CH_4 fluxes on the order of 10^1–10^2 mg m^{-2} day^{-1}, and heavier alkanes (ethane, propane, butane, and pentane) and benzene were also detected. Laboratory analyses confirmed that the gas has a dominant thermogenic origin, likely with a minor microbial component (the "Bernard ratio $C_1/(C_2 + C_3)$ was determined to be 23 and the stable carbon isotopic composition of CH_4, $\delta^{13}C$, was −57 ‰; see the notations in Chap. 1 and Fig. 1.2). The hydrocarbons likely migrate from productive reservoirs in Miocene reef limestones (Reeves 1953).

A discussion is provided in Chap. 7 regarding springs in serpentinised ultramafic rocks that may carry methane of abiotic origin.

2.1.4 Mud Volcanoes

Mud volcanoes are the largest surface expression of the migration of hydrocarbon fluids in petroleum bearing sedimentary basins (Fig. 2.5). Geology and formation mechanisms are described in a wide array of scientific literature (e.g., Milkov 2000; Kopf 2002; Dimitrov 2002a). Only some of the basic concepts are outlined here.

Mud volcanoes are cone shaped structures produced over faults by the upwelling of sediments (mud) fluidised by gas and water; and may develop as single isolated cones and craters or, more frequently, as groups of cones and crater systems. The diameter of single craters may range from a few cm to several tens of meters and conical structures can be several hundreds of meters high, as for the giant mud volcanoes of Azerbaijan (Fig. 2.5).

Gas is typically released from craters, gryphons (gas-mud vents generally occurring at the flanks of a main dome or crater; Fig. 2.6), or bubbling pools and small lakes (salses; Fig. 2.7) and, as for other types of macro-seeps, through the diffuse exhalation (miniseepage) of muddy ground (Table 2.1). Some mud volcanoes are characterised by intense and continuous degassing through gryphons and salses while others have low or absent venting activity but higher eruptive potential. Eruptions of gas and mud can be explosive and can represent a hazard for local communities and infrastructures (see Chap. 6). From 1810 until present, more than 250 eruptions of 60 mud volcanoes have been observed in Azerbaijan. Some have released tens of thousands of tonnes of CH_4 within a few hours (e.g., Guliyev and Feizullayev 1997).

Mud volcanoes are formed in sedimentary basins and involve the mobilisation of sedimentary rocks, mainly shales. Accordingly, they can be considered as a type of "sedimentary volcano" (not to be confused with traditional volcanoes, which are related to magmatic processes). Some confusion, however, exists within the

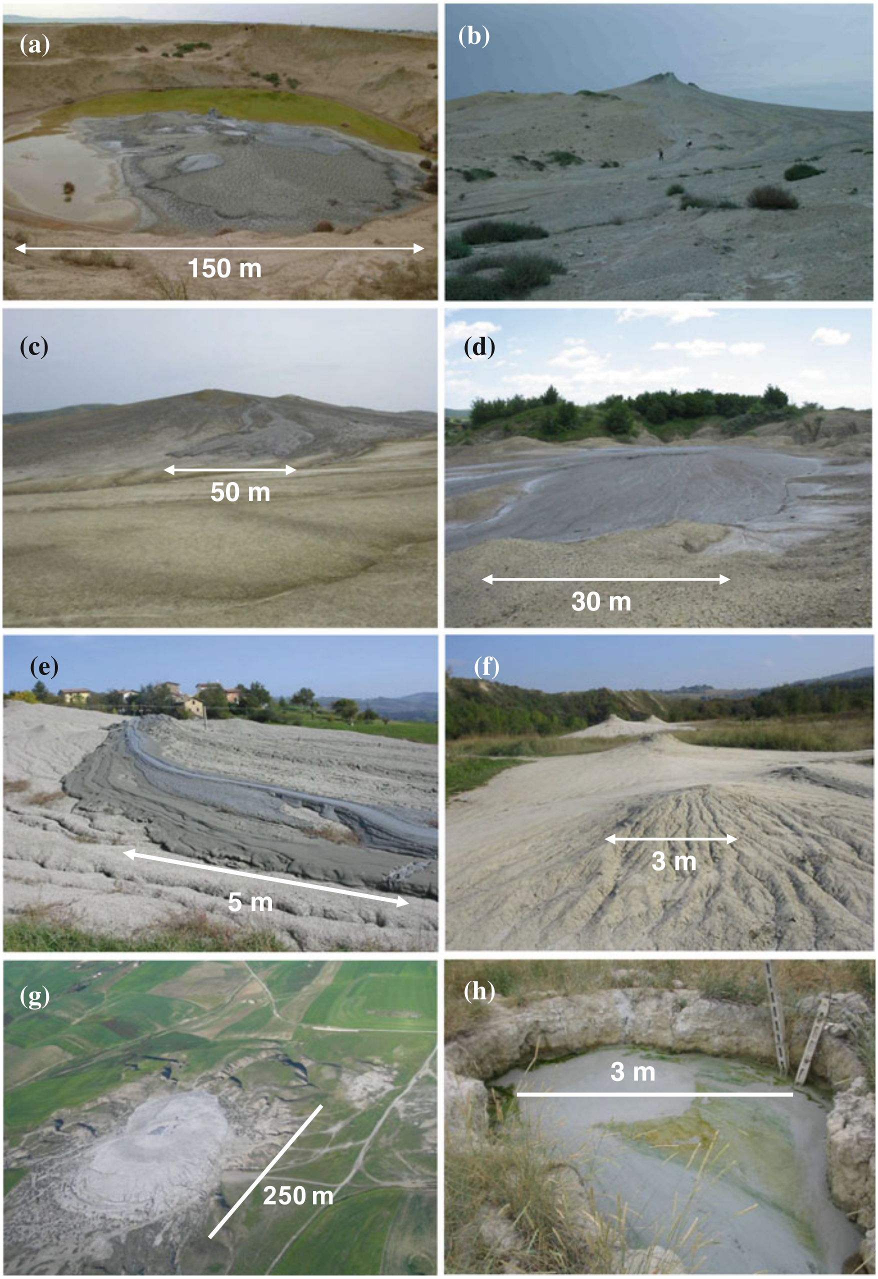

Fig. 2.5 Mud volcanoes **a**, **b** Bakhar New and Bakhar, Azerbaijan; **c** Paclele Mari, Romania; **d** Fierbatori, Romania; **e** Regnano, North Italy; **f** Nirano, North Italy; **g** Maccalube, Sicily, Italy; and **h** Pineto, Central Italy. (*Photos credits* **a**, **b** L. Innocenzi INGV; **c**, **d**, **e**, **f** and **h** G. Etiope; **g** courtesy of www.iloveagrigento.it)

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