Chapter 4
Detecting and Measuring Gas Seepage

This chapter provides a representative overview of current methodologies for detection of gas seepage on Earth's surface, both on land and in aquatic environments (rivers, lakes, oceans). Most of the techniques described can be utilised to discover gas seepage independent of the study objective (i.e. whether for petroleum exploration, geo-hazards, or environmental studies). Most of these techniques can also be used to measure anthropogenic gas leaks, such as fugitive emissions from petroleum production and distribution facilities. Applications to petroleum exploration, as well as related interpretative tools and limits, with references to microseepage detection, are discussed in Chap. 5.

The goal of this chapter is not (and cannot be) an exhaustive manual or review for all of the currently available surface seepage prospecting methods. As outlined in the sections below, several traditional techniques have been described in review papers. Here, a synthetic and synoptic picture for several currently available methodologies is provided, including the latest techniques and capabilities offered by new generation instruments. The discussion provided here focuses on direct gas detection methods. The use of gas seepage in petroleum exploration is outlined in Chap. 5. Indirect methods, including geophysical techniques and measurements of chemical, physical, or microbiological parameters in soils, water, rocks, or vegetation, modified by the presence of hydrocarbons, are briefly illustrated. Specific references, as well as a few case histories, are provided for those interested in a deeper reading of the technical details of sensing principles and instrumentation design. The detection of oil is not the objective of this book.

4.1 Gas Detection Methods

As illustrated in Fig. 4.1, gas seepage can be detected above the ground (atmospheric measurements), in the ground (soils and well head-space), and in water bodies (shallow aquifers, springs, rivers, bogs, lakes, and seas). Several of the methodologies are visually reviewed in the tree diagram shown in Fig. 4.2.

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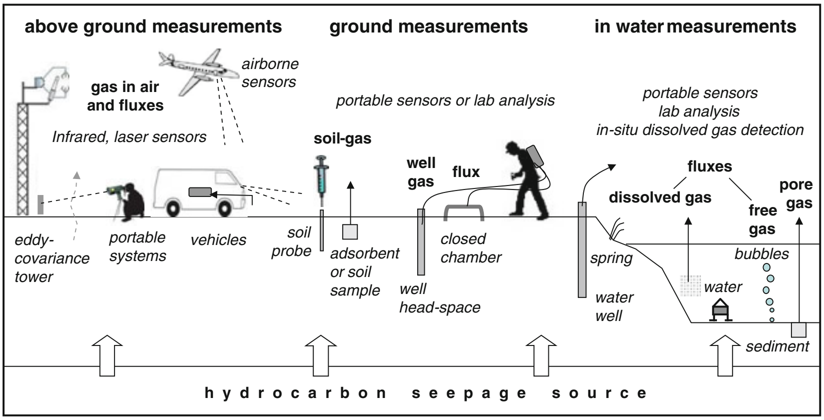

Fig. 4.1 Primary techniques used for direct gas seepage detection, sampling, and analysis in the atmosphere, in the ground or at the ground-atmosphere interface, and in aquatic systems (springs, lakes, bogs, rivers, and seas)

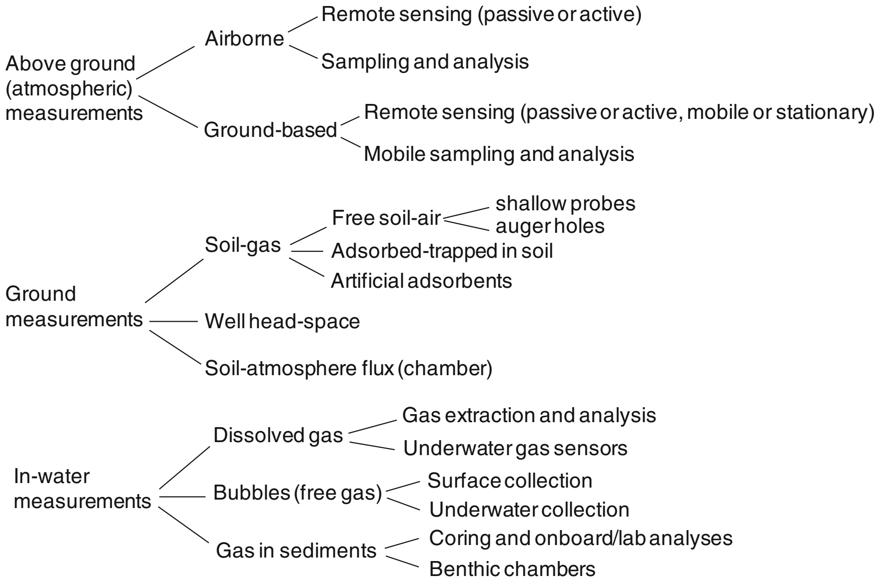

Fig. 4.2 Main methodologies of seepage detection using direct gas measurements

4.1.1 Above-Ground (Atmospheric) Measurements

Detecting hydrocarbons above the ground's surface has several advantages but also comes with substantial drawbacks. Measuring gas in the atmosphere may not require special permits; soils, either in natural or agricultural fields, are not disturbed, and gas samples representing average signals from large areas can be sampled rapidly. However, depending on the distance from the seepage source, wind and advective mixing in the atmosphere can significantly decrease a gas seepage signal's strength. As a result, detecting seeping gas strongly depends on weather conditions. In many cases, methane dispersion, even for intense seepage to the atmosphere, may lead to column average concentrations that are very close to or only slightly above background levels. Any specific gas concentration anomaly should be verified and confirmed based on ground-based and local measurements. Hydrocarbons detected in the atmosphere can, in fact, result from anthropogenic or natural sources not related to gas seepage (e.g., wetlands, landfills, fossil fuel plants, and leaking pipelines). However, technological improvements over the last twenty years have led to an increase in the capability for detecting trace amounts of gases from/in the atmosphere. Airborne methods are only of practical use for detecting relatively large gas emissions from macro-seeps. Microseepage is more easily detected using ground-based measurements.

Gas detection instrumentation can be divided into two main classes, remote sensing and air-sampling systems, and both can be operated from airborne or ground-based platforms or vehicles.

4.1.1.1 Remote Sensing

The remote sensing of gas in the lower atmosphere is based on analyses of radiation absorbed and emitted by gas molecules. Thus, instruments are generally based on absorption optical spectroscopy. Methane has strong rotational-vibrational transitions that cause absorption in the near-infrared (NIR, 0.78–3 μm wave length) and mid-infrared (MIR, 3–50 μm) spectral ranges, at wave lengths of 1.65, 2.35, and 3.4 μm. Remote sensing can be passive (observations of radiation naturally reflected by gas molecules) or active (observations of radiation reflected or backscattered by gas molecules following laser beam scanning), and can be obtained from satellites (remote sensing from space), aircraft, helicopters, drones (airborne remote sensing), ground-based vehicles, or portable hand-held sensors. At present, available satellite-based remote sensing systems (e.g., SCIAMACHY and GOSAT; Buchwitz et al. 2010) are only capable of detecting continental-scale variations in CH_4 (and other non-hydrocarbon gases such as CO_2 and N_2O). These systems have spatial resolutions up to 10 km (GOSAT), too large for the detection of near-surface local emissions or gas plumes from concentrated point sources. As a result, they are not effective for local scale gas seepage detection. Airborne systems have a much higher resolution and are capable of determining local scale emissions. Recent examples of passive airborne imaging spectrometry applied to gas seepage include the Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) (Bradley et al. 2011; Thorpe et al. 2013) and the Methane Airborne MAPper (MAMAP) instrument (Gerilowski et al. 2010), working in the short-wave infrared (SWIR) and near-infrared (NIR) portions of the electromagnetic spectrum. AVIRIS has been applied to marine and terrestrial seeps in California including the Coal Oil Point marine seep field (Bradley et al. 2011). In the study of Bradley et al. (2011), remote sensing seep anomalies were found to be consistent with the rising bubble plumes observed on site. The technique is well-suited for the detection of methane seepage from point sources over large areas, but false positives can result from surfaces with strong absorptions at the same wave lengths as those for methane, such as carbonates (2.35 μm).

Active systems for gas seepage detection are based on LIDAR (light detection and ranging) systems (e.g., Zirnig 2004; Thomas et al. 2013) used either in airborne or ground-based platforms, and portable open-path tunable diode laser (TDL) sensors that can easily be handled by one operator. Differential Absorption LIDAR (DIAL), in particular, uses a pulsed laser operating at two wavelengths, one strongly absorbed by the gas (MIR at 3.4 μm) and one weakly absorbed. Differential absorption is proportional to the gas concentration. DIAL was successfully used to detect gas leaks from pipelines (Zirnig et al. 2004). Examples of portable open-path laser sensors are the Boreal Laser's GasFinder (e.g., http://www.epa.gov/etv/pubs/01_vs_boreal.pdf) and Lasermethane™ (Tokyo Gas Engineering and Anritsu Corp.) which is based on wavelength modulation absorption spectroscopy (Iseki 2004). The Lasermethane™ sensor was used to rapidly detect microseepage methane anomalies in air (>2 ppmv), a few cm above the soil, by manually directing a laser beam across tens of meters in the field (Fig. 4.3). Wide areas can be scanned over a short period of time (a 0.3 km^2 field can be scanned within 1 h), by recognising the existence of microseepage in wide zones, with anomalies of up to 40–50 ppmv of methane approximately 10–20 cm above the soil (Etiope and Klusman 2010). Using the ground as a reflector, the instrument has also been used to detect gas leaks from soils or rocks (Etiope et al. 2006).

Fig. 4.3 Detection of anomalous concentrations of methane in the air a few centimetres above the ground using a portable laser sensor (Fierbatori seepage area, Berca oil-field, Romania; photo by C. Baciu)

4.1.1.2 In Situ Sampling-Analysis Systems

Aircraft, helicopters, or ground vehicles can mount “sniffing” devices that collect and pump atmospheric air towards gas sensors. High resolution spectrometers based on Cavity Ring-Down Spectroscopy (CRDS), NonDispersive InfraRed (NDIR), Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS), and Tunable Diode Laser Absorption Spectroscopy (TDLAS) (e.g., Hirst et al. 2004; Chen et al. 2010; Baer et al. 2012) are capable of detecting trace amounts (ppbv or ppmv) of light hydrocarbons (mainly methane and ethane) in excess of background atmospheric concentrations. Air samples can also be collected and stored for laboratory analyses. The sampling location is recorded by a Global Positioning System (GPS) navigation system that is generally interfaced to the gas analyzer or sampler. As for remote sensing, wind and ground conditions can strongly dilute hydrocarbon flow to the atmosphere and humidity can delay or reduce the gas rising to flight altitudes. Examples of atmospheric ground-based surveys for gas seepage detection can be found in LTE (2007) and Hirst et al. (2004). By driving along roads for 4,490 km in the Raton Basin in Colorado, 67 seep locations were found by analysing air with a fast IR analyser mounted at approximately half a meter from the ground in the rear of a car while recording atmospheric CH_4 anomalies of up to 700 ppmv (LTE 2007).

Stationary atmospheric measurements are typically made using micrometeorological towers, such as those employed for the Eddy-Covariance (EC) method (Burba et al. 2010). The EC method allows estimations of gas flux from the ground to the atmosphere based on rapid sequential gas measurements (by high-resolution infrared sensors), vertical temperature gradients, and air velocities measured in three-dimensions using a sonic anemometer. The method is mainly employed in studies of biological CO_2, CH_4 and ammonia (NH_3) emissions and surface ecosystem budgets, and rarely used to investigate geological gas emissions (e.g., Lewicki et al. 2009).

Mobile surveys based on air sampling and gas chromatography/mass spectrometric (GC/MS) laboratory analyses are described in Petron et al. (2012). The study was not aimed at detecting natural seepage but at assessing man-made hydrocarbon emissions at petroleum production and processing sites. The air-sampling approach may allow the simultaneous detection and quantification of a large number of gas species released by natural seepage (virtually all gaseous hydrocarbons and associated non-hydrocarbon gases), and, for a better understanding of their origin, different types of isotopic analyses. Data points obtained in this manner are obviously discontinuous and widely spaced and could miss seepage signals occurring at non-sampled sites, which could be captured using continuous measurements.

4.1.2 Ground Measurements

Ground measurements include all of the methods capable of detecting gas in the soil or the shallow sub-soil, and at the soil-atmosphere interface (Fig. 4.1). These measurements also include gas in well head-space, and gas flux from soil to the atmosphere. Gas in all of these systems can be analysed in the laboratory following convenient and economical storage of gas in vials or bags, or analysed directly on site using portable hand-held sensors. In addition to traditional portable gas-chromatographs (with Flame Ionization Detectors, FID, or Thermal Conductivity Detectors, TCD), today, fast and sensitive analysers based on closed-path IR lasers or cavity enhanced absorption sensors are available for detecting methane at sub-ppmv levels. Measuring gas directly on site allows the immediate recognition of seepage and drives surveying strategies, leading to the selection of measurement points. Ground measurements are the most effective method for detecting and characterising low gas exhalations related to microseepage.

4.1.2.1 Soil-Gas or Subsoil Pore-Gas Analysis

Measuring gas composition and concentration in the soil is likely the most employed method for detecting and characterising hydrocarbon seepage. Measurements can be performed on the free gas in soil pores (soil-air), or on the gas trapped in poorly permeable soil or adsorbed to soil minerals or artificial adsorbents that are inserted into soils or sediments.

Free soil-gas can be accessed via shallow (generally around 1 m) metal probes manually inserted into the soil, or via deeper auger holes (generally up to depths of 3–4 m). The gas can be extracted using syringes or manual pumps, and analysed on site using portable sensors or stored in bags or vials for subsequent laboratory analyses. Shallow probe sampling is much more rapid and economical, as may allow complete gas sampling/analysis within a few minutes. However, the shallower the sampling and the higher the soil's porosity and permeability (as for dry sands), the lower the amounts of hydrocarbon gas that can be detected since soil-air may become diluted by advected atmospheric air. Deeper holes almost always encounter water, which also influences the collection of free gases. Water-logged soil and mud should be avoided. The concentration of seeping gas in soil-air is then controlled by meteorological factors such as atmospheric pressure, temperature, and precipitation, as discussed in a wide array of scientific literature (e.g., Klusman and Webster 1981; Hinkle 1994; Wyatt et al. 1995).

Hydrocarbons are generally also trapped in small soil pores or loosely bound to soil grains, organics, or minerals, and cannot be quantitatively extracted using soil probes. Soil samples can be directly collected using special containers that, after heating or shaking, form a head-space from which gas can be sampled and analysed. The main problem with this approach is limited sample integrity and gas lost during drilling and laboratory treatments. In agricultural fields, samples may also be contaminated by fertilizers, herbicides and insecticides containing hydrocarbon-based additives that may confound the search of heavy hydrocarbons related to natural seepage.

Hydrocarbons reaching the B-horizon in soil can adsorb onto clays or become occluded within carbonate cements. Desorption through heating and acid extraction procedures allow hydrocarbon GC analyses that can detect more than a hundred different compounds, generally from C_5 to C_{20}, at the ppb and ppt levels (e.g., Philp and Crisp 1982, and references therein). However, results strongly depend on the type of soil sampled, the presence of diagenetic carbonates that may release hydrocarbons independent of seepage, and humidity and pH conditions. Acidic soils do not produce carbonate cement, so hydrocarbons cannot be occluded.

An alternative to soil sampling is provided by artificial adsorbents, such as activated carbon (e.g., Klusman 2011) or microporous materials housed in chemically inert, hydrophobic, polytetrafluoroethylene (Teflon®) membranes (e.g., http://www.epa.gov/etv/pubs/01_vr_goresorber.pdf). Adsorbents are typically installed at a depth of 0.5–1 m and passive soil-gas sampling may last for several weeks. The lightest detectable hydrocarbon is ethane. Methane cannot be adsorbed. The main advantage of this technique is that it integrates the gas concentration over long periods by removing the variability caused by atmospheric changes.

Soil-gas prospections for gas seepage detection have been widely documented in the scientific literature. Jones and Drozd (1983), Richers et al. (1986), Richers and Maxwell (1991), Dickinson and Matthews (1993), Jones et al. (2000), Harbert et al. (2006), Klusman (2006), Mani et al. (2011), and Sechman (2012) are just a few examples of peer-reviewed publications.

4.1.2.2 Well Head-Space Analyses

Wells drilled for different purposes, such as shallow explorations, stratigraphic boreholes, water wells, or piezometers, can be used for local collection of gas from seepage. If the well-head is accessible (by opening the cap or valves), the head-space above the water table can be sampled for laboratory analyses or directly analysed on site using portable sensors. The head-space may contain hydrocarbon gases exsolved from the water, or those crossing the aquifer and the water column in the well, as bubbles. Within the Po Basin in northern Italy, numerous wells have high hydrocarbon concentrations within the well head-space and some have been used to assess the origin of gas seepage in the region (e.g., Etiope et al. 2007).

4.1.2.3 Soil-Atmosphere Gas Flux Measurements

The flux of natural gas from the soil to the atmosphere is an important parameter in seepage studies because in addition to information on the presence of gas seepage it provides an indication of intensity and persistence, reflecting underground gas pressures, gas flux, and accumulation potential. The main technique adopted for measuring gas flux in the ground is that of the closed or accumulation chamber, a well-established, economical, and straightforward technology (Fig. 4.4).

The technique allows gas flux calculations by measuring gas concentration build-up (accumulation) over time inside a chamber that is firmly positioned on the surface. If the rate of change of gas concentration is constant (steady emission, i.e., ppmv versus time is linear) then linear regression can be used in order to calculate

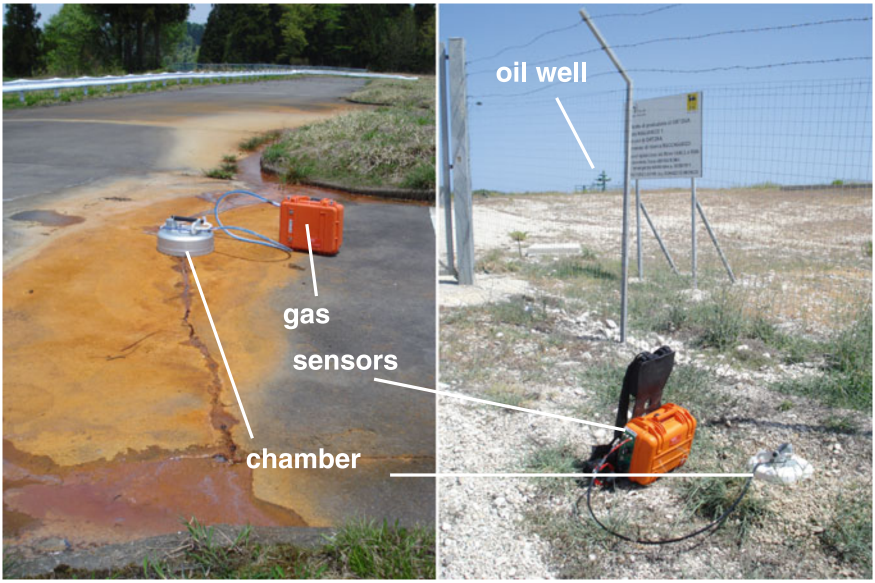

Fig. 4.4 Examples of gas flux measurements using the closed-chamber method with portable gas sensors. *Left* gas seepage through the asphalt at Tokamachi (Niigata Basin, Japan); *Right* a microseepage measurement at the Miglianico oil field in central Italy (also see Sect 5.2 and Fig. 5.2). Photos by G. Etiope

the slope of concentration versus time. The slope of the line reflects the gas flux. The flux, Q, is obtained by multiplying the slope by the chamber height (m), and is generally expressed in terms of mg m^{-2} day^{-1}, as follows:

$$Q = \frac{V_{FC}}{A_{FC}} \cdot \frac{c_2 - c_1}{t_2 - t_1} \left[\frac{\text{mg}}{\text{m}^{2*}\text{d}}\right]$$

where V_{FC} (m^3) is the volume of the chamber, A_{FC} (m^2) is its area, and c_1 and c_2 (mg/m^3) are the methane concentrations at times t_1 and t_2 (days). Measurement times are chosen depending on the gas flux and the sensitivity of the analyser. The lower the gas flux, the higher the time required to obtain a measurable gas concentration. The lower the height of the chamber, the lower the time required to measure a given flux. For example, for a sensor with a resolution and a lower detection limit of 1 ppmv CH_4, a methane flux of 100 mg m^{-2} d^{-1} can be measured in 1 min using a chamber with a height of 10 cm; 30 s for a chamber of 5 cm.

Methane concentrations can be measured in the laboratory after a gas is collected in vials or bags, or on site using portable sensors. On-site analyses with portable flow-through sensors allow for continuous recording of concentration build-up. Imperfect sealing of the chamber's bottom against the ground may lead to underestimations of flux measurements. Uncertainty for measurements is, therefore, related to the errors (accuracy and reproducibility) of the analyser itself and to the actual volume of air enclosed by the chamber, which depends on how deep within the soil the chamber is actually positioned.

Closed-chambers can be used for short-term measurements and spatial surveys, and for long-term monitoring in fixed positions. Several authors have provided basic recommendations and guidelines regarding the use of closed-chambers (e.g., Mosier 1989). The main potential problems include temperature perturbations (influencing biological activity and gas adsorption into soil minerals) and pressure perturbations induced by wind (causing deviations in mass flow in and around the chamber). Such problems can be minimised using insulated, reflective chambers equipped with a capillary hole capable of equilibrating the internal and external air pressure.

Closed-chambers were initially developed for studies of the exchange of carbon and nitrogen bearing gases at the soil-atmosphere interface, such as for soil respiration (e.g., Hutchinson and Livingston 1993; Norman et al. 1997). The technique was then applied to detect methane microseepage in petroliferous basins (Klusman et al. 2000; LTE 2007) and coal mines (Thielemann et al. 2000), and gas exhalations in geothermal or volcanic areas (e.g., Hernandez et al. 1998; Etiope 1999; Cardellini et al. 2003). A wide array of reports of chamber measurements for methane fluxes in mud volcanoes and other types of seeps are currently available (e.g., Etiope et al. 2004a, b; 2011a, b; 2013; Hong et al. 2013). Such studies have allowed the recognition of invisible miniseepage (see the definition in Chap. 2) surrounding vents at macro-seepage sites (Fig. 4.4). The closed-chamber method has also been fundamental for assessing the typical methane fluxes for various types of seeps, as described in Chap. 2, and, based on the procedures described in Chap. 6, for deriving local, regional, and global bottom-up estimates of geological methane emissions to the atmosphere.

4.1.3 Measurements in Aqueous Systems

Hydrocarbons in the waters of lakes, bogs, rivers, springs, shallow aquifers, and seas can occur in solution (as a dissolved gas) or as a free-phase (bubbles). Seeping gas is then present within sediments.

4.1.3.1 Dissolved Gas

Water samples from aqueous environments can be collected in glass bottles properly sealed with hydrocarbon-free septa and secured with aluminium caps. Deep waters in lakes and seas can be collected using Nansen or Niskin bottles then stored in glass bottles. The addition of a microbicide (e.g., mercuric chloride, $HgCl_2$) is useful for limiting methane oxidation. Dissolved gases can then be extracted either on site or in the laboratory using head-space and/or stripping methods (McAuliffe 1969; Capasso and Inguaggiato 1998).

In offshore petroleum exploration areas, seawater can be pumped from a ship through deep towed sample inlets at depths of 100–200 m and carried to an onboard analysis system (e.g., Sackett 1977; Philp and Crisp 1982; Gasperini et al. 2012). Gases in solution can then be stripped from seawater samples and analysed via gas-chromatography or other sensors.

Methane can also be directly analysed in solution using special underwater sensors that employ a semi-permeable membrane that allows gas permeation into an internal head-space in contact with a detector, generally a solid-state, optical sensor or spectrometer. Such instruments are typically employed in the marine environment, in vertical casts, in horizontal profilers, or in benthic platforms (e.g., Marinaro et al. 2006; Camilli and Duryea 2007; Newman et al. 2008; Krabbenhoeft et al. 2010; Gasperini et al. 2012; Embriaco et al. 2014). A review of the present technology is provided in Boulart et al. (2010).

4.1.3.2 Gas Bubble Collection

Bubble trains observable at the surface of lakes, rivers, bogs, seawater and in water pools of mud volcanoes can be captured using special funnels ("bubble traps") or floating accumulation chambers that can also measure gas flux (e.g., Cole et al. 2010; Etiope et al. 2013). Bubble traps are initially purged using water that is progressively displaced by gas. Since the volume of the funnel is known, the time bubbling gas takes to displace water can provide a good estimate of the gas flow rate. In vents not accessible for direct measurements, the order of magnitude of the gas flux to the atmosphere from bubbles can be visually estimated by examining the size and frequency of individual bubble trains (Etiope et al. 2004a, b). For example, the gas output of a single train of spherical bubbles with diameters of 1 cm (0.5 mL), having 80 % CH_4 and bursting each second, is in the order of 40 L per day.

Bubbles can be collected underwater, along the water column or on the floor, by a diver (e.g., Etiope et al. 2006) or by remotely operating vehicles equipped with arms and special sampling tools (e.g., Bourry et al. 2009). In all cases, the sampled gas can then be analysed in the laboratory for a complete molecular and isotopic composition. However, due to the exchange of gas species between the bubbles and seawater, as outlined in Chap. 6, it is important to understand that the gas composition of bubbles at the sea or lake surface, having travelled several tens or hundreds of meters along the water column, may be different from the original gas issuing from the sea or lake bottom.

4.1.3.3 Underwater Sediment Analyses

Gas-charged sediments located on the bottom of lakes, rivers, and seas can be sampled using several types of tools based on gravity driven or rotary mechanical penetration (e.g., Hopkins 1964; Abrams 2013). Gravity corers consist of a hollow tube (the barrel with a core liner) attached to an external weight. Mechanical coring devices use rotary drilling or vibracoring to facilitate the penetration of the barrel into sediments. Vibracorers, in particular, are effective in sampling compacted and slightly cemented sediments that cannot be penetrated using conventional gravity driven devices (Abrams 2013). Once a sediment sample is retrieved onboard a ship, it must be quickly processed and stored for successive laboratory analyses. Since they can be rapidly lost, volatile hydrocarbons (C_1–C_{12}) and non-hydrocarbon gases require special handling. Sediments are typically stored in non-coated metal cans or clear plastic jars. Seawater and an inert gas (helium) or air are added to create a head-space. To prevent hydrocarbon oxidation by microbes, anti-microbial agents, such as sodium azide or mercuric chloride, must be added before closing the can or jar. Technical details regarding sediment sampling and analyses have been reported in a wide array of scientific literature and reviews, including Bernard et al. (1978), Logan et al. (2009), Abrams and Dahdah (2010), Abrams (1996, 2013), and references therein.

Benthic chambers have also been used to detect gas seepage from lakes or marine sediments (e.g., Caprais et al. 2010). These chambers work like soil-atmosphere flux chambers and use sampling cells that collect small amounts of water at predetermined intervals. Chambers can be deployed and recovered using remotely operated vehicles or divers in shallower waters.

4.2 Indirect Methods

Indirect methods for seepage detection are based on the recognition of chemical, physical, and biological changes in soils, sediments, rocks, vegetation, or water, that are induced by the presence of hydrocarbons or other gases related to seepage. Changes include those associated with microbiology, minerals, acoustics, electro-chemistry, radioactivity, and vegetation anomalies. The synoptic tree diagram provided in Fig. 4.5 summarises the main methods, briefly described below. The scheme refers to gas seepage detection, not oil detection or underground reservoir research. For technical details, applications, and case histories, the reader should consult the references provided below.

Although indirect methods alone are not sufficient for identifying underground hydrocarbon resources of commercial importance, most, especially those based on remote sensing, have allowed us to discover hydrocarbon seepage throughout large areas in sedimentary basins, suggesting that microseepage is a ubiquitous process in petroleum systems as discussed in Chap. 2.

4.2.1 Chemical-Mineralogical Alterations of Soils

Hydrocarbons can modify certain chemical and mineralogical features of soils. Microbial biodegradation entails hydrocarbon oxidation, particularly of methane, and may produce diagenetic carbonates, typically calcite. The process is the same as

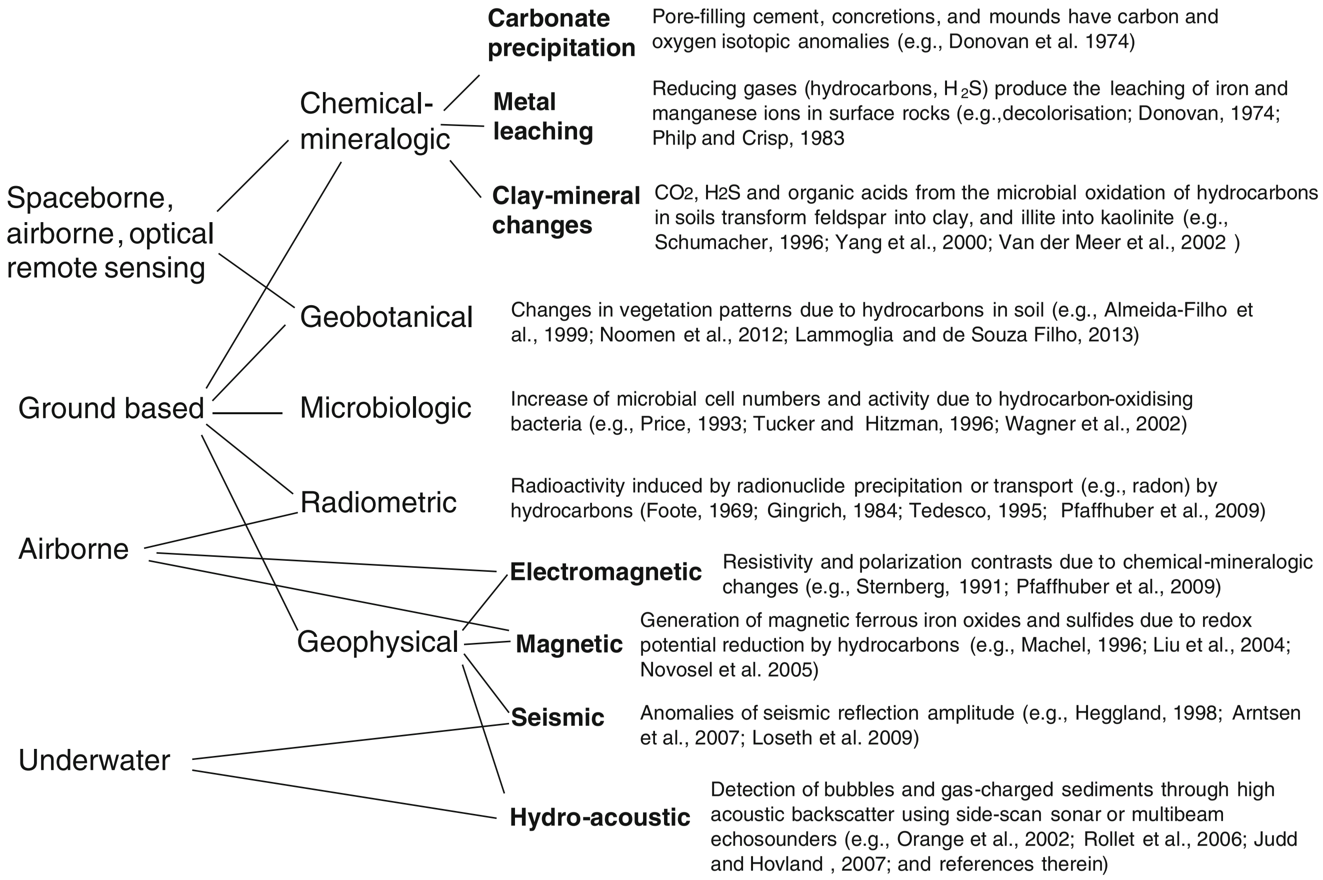

Fig. 4.5 Main indirect methods of natural gas seepage detection

the one described in Chap. 2 that produces carbonates on the seafloor. Calcite fills soil pores and the oxidation is generally aerobic, as follows:

$$CH_4 + 2O_2 + Ca^{2+} = CaCO_3 + H_2O + 2H^+$$

The reaction evolves via the production of carbon dioxide that reacts with water to form bicarbonate. The produced bicarbonate precipitates as carbonate or carbonate cement with a $^{13}C/^{12}C$ isotopic ratio (expressed as $\delta^{13}C$ value along the VPDB carbon isotopic scale in permil) that is related to that of the biodegraded parent hydrocarbon. Calcite formed in this manner typically has an isotopic composition more negative than –20 ‰ that is much lower than the traditional calcite derived from the atmosphere, freshwater, or marine environments (of approximately –10 to +5 ‰). Diagenetic methane-derived carbonates in soils are widespread, in correspondence with many petroleum fields in North America, as documented, for example, by Donovan et al. (1974) and Schumacher (1996).

Additionally, hydrocarbons and associated hydrogen sulphide (H_2S) can reduce ferric oxide (hematite) and manganese ions in soil minerals and sandstones, forming bleaching red beds, or, in general, the decolorisation of rock. Sandstones are generally unaltered, reddish-brown, outside the boundary of petroleum fields, and may become pink, yellow, and white along the faults of productive anticlines (Donovan 1974). CO_2, H_2S, and organic acids from the microbial oxidation of hydrocarbons in soils can also transform feldspar into clay, and illite to kaolinite (e.g., Schumacher 1996). Alterations can effectively be detected using optical remote sensing techniques such as aerial photography, radar, a Landsat Multispectral Scanner, a Landsat Thematic Mapper, or airborne multispectral scanner data (Yang et al. 2000; van der Meer et al. 2002).

However, it is important to understand that although the mechanisms of the soil alterations induced by seeping hydrocarbons are well established, the cause of soil and sediment alteration in a given area may not be due to hydrocarbon seepage. Many factors other than seepage can induce near-surface anomalies. Hydrocarbons can be an indirect cause, but are not always the most likely cause. Therefore, the prospection methods outlined below are not conclusive, but are useful for reconnaissance surveys. In association with direct gas detection methods, these methods can effectively support and complete interpretations derived using traditional geophysical techniques of petroleum exploration.

4.2.2 Vegetation Changes (Geobotanical Anomalies)

Hydrocarbons in the soil may impact vegetation growth and health, and can be detected through the analysis of reflectance spectra (Almeida-Filho et al. 1999; Noomen et al. 2012; Lammoglia and de Souza Filho 2013). The reflectance of healthy vegetation can be observed using visible light based on the absorption features caused by plant pigments such as chlorophyll and carotenoids, and in the near infrared (NIR) and shortwave infrared (SWIR) using adsorption bands related to internal leaf structure, water content, and leaf area. The cause of vegetation modification is generally related to oxygen depletion in soil induced by the presence of hydrocarbons, but plant growth can also be directly affected by hydrocarbons when ethane concentrations within the soil are greater than 0.7 vol.% (Noomen et al. 2012). The two main biological indicators of gas seepage are decreases in chlorophyll abundance and leaf area.

4.2.3 Microbiological Analyses of Soils

Hydrocarbon-oxidising bacteria are specialised microorganisms that take energy from hydrocarbon gases and liquids. Microorganisms can use extremely low concentrations of hydrocarbons and are typically found living within soils and seabed sediments above hydrocarbon reservoirs (e.g., Price 1993; Tucker and Hitzman 1996; Wagner et al. 2002). Wherever small traces of hydrocarbons occur during a period of several years in the soil, there is a significant occurrence of specialised bacteria (Hanson and Hanson 1996). Onshore sampling is performed using a hand auger at a depth of ~150 cm. Offshore samples are obtained using a vibracorer or grab sampler, at approximately 30 cm below the top of the sediment. Samples are then packed in airtight sterile bags and transported to the laboratory for the incubation and specific analyses of total cell counts and microbial activity (consumption of hydrocarbons using gas chromatography and pressure measurements, and biological CO_2 formation rates). Numerous case-histories exist for microbiological prospections devoted to petroleum exploration (see, for example, Wagner et al. 2002 and references therein).

4.2.4 Radiometric Surveys

The occurrence of radionuclides, such as uranium and radium, in hydrocarbons is widely documented within the petroleum geochemistry literature (e.g., Durrance 1986; Hunt 1996). Radionuclides accumulate in petroleum deposits due to anoxic environments and chelation by organic molecules. Of sedimentary rocks, productive petroleum-bearing shales contain the highest levels of radioactivity. Hence, hydrocarbon fluids can be more radioactive than other fluids, leading to an assumption that hydrocarbon seepage can be detected by relatively high concentrations of radionuclides within the near surface which is only partially true. Petroleum accumulations almost never produce high radioactivity at the surface. To be more precise, the total gamma radiation produced is not necessarily high above hydrocarbon accumulations. Only concentrations (or better the activity) of radon-222, the gaseous radionuclide in the nuclear decay chain of uranium-235, are typically higher in soils above petroleum fields (Gott and Hill 1953; Foote 1969;

Gingrich 1984; Pfaffhuber et al. 2009). The relative concentration of different radionuclides, whose behaviour (and migration capability) is different in relation to the redox conditions in rocks, is important. A column of rocks impacted by hydrocarbon seepage is, in fact, a reducing environment. Rocks without hydrocarbons generally exist under oxidising conditions. Some radionuclides are mobile under reducing conditions while others are not. The use of radioactivity for petroleum exploration has always been controversial, mainly because past measurements were based on total gamma radiation without differentiating various radionuclides. Therefore, although the method still has some proponents and has apparently been used with some success in Russia, it has met with little acceptance in the petroleum industry due to an insufficient understanding of its technical basis and because different techniques did not work consistently. That radiometric survey should be executed with spectrometers capable of measuring total radioactivity and differentiating radionuclides, and not radiometers, which provide only total gamma radiation, is important. Knowing specific ratios between selected radionuclides is, in fact, necessary for revealing the presence of seepage in soils or seabed sediments.

During hydrocarbon gas microseepage, micro-sized bubbles of gas seep near-vertically through a network of water filled joints and bedding planes immediately above hydrocarbon deposits. Carbonic and organic acids transform the clay minerals, primarily illite, that contain potassium and uranium. As a result, these elements are released and leached away by groundwater. The uranium may not leach away entirely but is chemically reduced to uraninite and precipitate, resulting in some build-up of uranium in surface sediments. The result explains the muted loss of uranium relative to potassium in the system. Thorium appears to be immune to these processes. Chemical reduction processes can also result in the development of magnetic minerals, leading to coincident "micromagnetic" anomalies. Radioelement anomalies over hydrocarbon microseepages typically have the following characteristics (e.g., Saunders 1993): 1. Potassium is significantly diminished. 2. Uranium is somewhat diminished and often variable. 3. Thorium remains relatively constant.

Additionally, a sort of electrochemical cell develops above reduced bodies (hydrocarbon accumulations) producing a very high contrast in the "oxidation suite" of minerals, including uranium and thorium. Apical radiometric anomalies may form over faults that act as a conduit for waters that contain radioactive minerals. However, halo anomalies are also found above the edges of reducing body (cathodes), with a central low over the centre of the body (anode).

Two processes, microseepage and the development of electrochemical cells (redox), produce low radionuclide responses over petroleum fields and/or high radionuclide responses surrounding the edges. In most cases, redox processes seem to prevail. Thus, the acquisition of high-resolution gamma ray spectrometer data, and careful data processing and enhancement for discriminating alteration effects from host lithologies, can provide viable exploration techniques. In summary, when subsurface hydrocarbons are absent, uranium's intrinsic migratory ability and its greater specific radioactivity cause it to be a significant contributor to the radiation detected at the surface. When hydrocarbons are present, geochemical interactions constrain or arrest uranium's movement, causing a decrease in the gamma flux detected over petroleum deposits. As such, low radiation flux patterns are distinguishable from the random gammas observed in areas barren of hydrocarbons. A decrease in total gamma-ray intensity, often observed over oil fields, may then be due to depletion in one or all three of the main radionuclides (^{40}K, ^{232}Th, and ^{238}U).

4.2.5 Geophysical Techniques

A wide set of geophysical methods can be used to detect seepage (not necessarily underground hydrocarbon accumulations), including electromagnetic, magnetic, seismic, and hydro-acoustic techniques, either onshore or offshore, from airborne, ground-based, or underwater systems (see Fig. 4.5). Due to the extent of the topic, this section is not exhaustive. Reviews are provided in Schumacher (1996) and Aminzadeh et al. (2013) and specific literature sources are found in Fig. 4.5. Only some of the basic concepts are provided here.

Magnetic and electromagnetic methods detect surface anomalies related to the mineralogical changes discussed above; for example, the production of magnetic ferrous iron oxide. These techniques are a natural complement of those that examine the ground's tonal anomalies. The link between hydrocarbons and magnetic anomalies was recognized at the beginning of the last century (Harris 1908), but extensive investigations have only been conducted in the USA since the late 1970s when a direct relationship between aeromagnetic anomalies and oil microseepage was determined over the Cement oil field in Oklahoma (Donovan 1974). In general, low magnetization is attributed to seepage. In fact, the reducing environment induced by seepage results in the diagenesis and transformation of highly magnetic minerals such as magnetite into nearly non-magnetic pyrite (Novosel et al. 2005).

Seismic methods, based on anomalies of seismic reflection amplitudes (e.g., Loseth et al. 2009), are a powerful tool for uncovering crustal seepage chimneys. In particular, 3D seismic data can provide 3-dimensional images of fluid flow shapes and their spatial distributions, including the seepage root (reservoir) and top (near surface or surface sediment modifications). Sesimic anomalies can be distinguished into the following two types: (1) permanent deformations of the primary bedding of sedimentary strata (e.g., mud mobilisations and sand injections) and the formation of surface or subsurface "syn-leakage" features (e.g., pockmarks, bioherms), and (2) acoustic changes due to the replacement of formation water by hydrocarbon fluids. Details and case-histories are well described by Heggland (1998) and Loseth et al. (2009), among others.

Finally, hydro-acoustic methods refer to the detection of acoustic backscatter related to gas bubbles (gas plumes or gas flares) rising within the water column, or to gas-charged sediments in rivers, lakes, or seas. Side-scan sonars and multibeam echosounders are typically employed and numerous examples exist for submarine seepage detection (e.g., Papatheodorou et al. 1993; Orange et al. 2002; Rollet et al. 2006; Judd and Hovland 2007; Weber et al. 2014 and references therein). These techniques allowed the development of important theoretical models for the transfer of methane from the seabed to the atmosphere and determined that, in general, gas only reaches the sea surface if the seep is shallower than 300–400 m (Schmale et al. 2005; McGinnis et al. 2006). Bubble acoustic scattering was also modelled in order to estimate the gas flux of a bubble plume, either from ship-based remote sensing (Weber et al. 2014) or from benthic landers (such as *GasQuant* or *BOB*, or the Bubble OBservatory module; Greinert 2008; Bayrakci et al. 2014). Benthic devices are particularly useful for monitoring seepage variations over time.

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