

# Chapter 4

## The Main Environmental Matrices: Air, Soil, and Water



### 4.1 Air Composition and Properties

Air, as an analytical matrix, presents itself as a vehicle of rapid dispersion of pollutants, much more than water, due to the high fugacity, or tendency to escape, of its gaseous constituents. The average composition of the atmosphere, which includes the air we breathe, is shown in Table 4.1.

The nitrogen and oxygen gases are the main constituents in volume, 78.1% and 20.9%, respectively. However, water vapor, carbon dioxide ( $\text{CO}_2$ ), and argon can also be observed in a more representative proportion in relation to the other gases present in much reduced concentrations. Carbon dioxide and methane ( $\text{CH}_4$ ) have attracted attention because of global warming—mainly the emission of carbon dioxide in the atmosphere via the burning of fossil fuel leading to an increase in temperature due to the absorption of infrared radiation (wavelength between  $10^{-6}$  and  $10^{-3}$  m). Methane from biochemical processes of biomass degradation can also produce this heating, due to the absorption of the same radiation.

Ozone ( $\text{O}_3$ ), as a constituent of the Earth's protective layer against ultraviolet radiation (wavelength between  $10^{-8}$  and  $10^{-6}$  m), also raises concern, since the decrease in its atmospheric concentration allows a higher incidence of this radiation, which can lead to skin cancer.

According to the World Health Organization (2006), some listed air pollutants raise greater care due to their toxic effects:

- Volatile organic compounds (VOCs): from the distribution of fuels, industries, vehicles, among others, are precursors of tropospheric  $\text{O}_3$ .
- Particulate matter: suspended particles, inhalable particles (diameter  $\leq 10 \mu\text{m}$ , called  $\text{PM}_{10}$ ), and combustion smoke cause respiratory complications.
- Carbon monoxide (CO): from vehicles and incinerators reduce the oxygen exchange capacity of the blood.
- Sulfur oxides ( $\text{SO}_x$ ): from combustion and incineration of coal and diesel oil cause acid rain.

**Table 4.1** Average composition of the atmosphere, according to Mirtov (1964)

Gaseous constituent	Percentage of volume (%)	Partial pressure (atm)
N <sub>2</sub>	78.1	0.781
O <sub>2</sub>	20.9	0.209
Ar	0.93	0.0093
H <sub>2</sub> O	0.1–2.8	0.028
CO <sub>2</sub>	0.03	0.0003
Ne	$1.8 \times 10^{-3}$	$1.8 \times 10^{-5}$
He	$5.2 \times 10^{-4}$	$5.2 \times 10^{-6}$
CH <sub>4</sub>	$1.5 \times 10^{-4}$	$1.5 \times 10^{-6}$
Kr	$1.1 \times 10^{-4}$	$1.1 \times 10^{-6}$
CO	$0.06\text{--}1 \times 10^{-4}$	$0.6\text{--}1 \times 10^{-6}$
SO <sub>2</sub>	$1 \times 10^{-5}$	$1 \times 10^{-6}$
N <sub>2</sub> O	$5 \times 10^{-5}$	$5 \times 10^{-7}$
H <sub>2</sub>	$5 \times 10^{-5}$	$5 \times 10^{-7}$
O <sub>3</sub>	$0.1\text{--}1 \times 10^{-5}$	$0.01\text{--}1 \times 10^{-7}$
Xe	$8.7 \times 10^{-6}$	$8.7 \times 10^{-8}$
NO <sub>2</sub>	$0.05\text{--}2 \times 10^{-5}$	$0.05\text{--}2 \times 10^{-8}$
Rn	$6 \times 10^{-18}$	$6 \times 10^{-20}$

- Nitrogen oxides (NO<sub>X</sub>): from industrial combustion processes and vehicles—NO<sub>2</sub> is the precursor of tropospheric ozone and acid rain.
- Tropospheric ozone (O<sub>3</sub>): formed when NO<sub>X</sub> and VOCs undergo photochemical reactions in the atmosphere in the presence of solar radiation; causes damage to the lungs, materials, and vegetation—not to be confused with the O<sub>3</sub> layer of protection against UV radiation.

Those compounds above cited are related to the outdoor pollution. When we consider the indoor pollution, we can observe the following (World Health Organization 2010):

- Benzene: originates from outdoor air and also from sources indoors such as building materials and furniture, attached garages, heating and cooking systems, stored solvents, and various human activities.
- Carbon monoxide: anthropogenic emissions are responsible for about two-thirds of the carbon monoxide in the atmosphere and natural emissions account for the remaining one-third. Small amounts are also produced endogenously in the human body. Exposure to low levels of carbon monoxide can occur outdoors near roads, as it is also produced by the exhaust of petrol- and diesel-powered motor vehicles. Parking areas can also be a source of carbon monoxide.
- Formaldehyde: combustion processes such as smoking, heating, cooking, or candle or incense burning. However, major sources in nonsmoking environments appear to be building materials and consumer products that emit formaldehyde.

This applies to new materials and products but can last several months, particularly in conditions with high relative humidity and high indoor temperatures.

- Naphthalene: it is used as feedstock in the manufacture of phthalic anhydride for the synthesis of phthalate plasticizers and synthetic resins. It is also used as feedstock for naphthalene sulfonic acids often used in the production of plasticizers for concrete, as ingredients for plasterboards, as dispersants in synthetic and natural rubbers, and as tanning agents in the leather industry. Naphthalene is also used in paints and in the production of the insecticide carbaryl, used in home yards and gardens. Still predominant in the exposure of consumers worldwide is the production and use of crystalline (pure) naphthalene as a moth repellent and disinfectant. Its use as a solid block deodorizer for toilets is also reported. Wood smoke, fuel oil, and gasoline also contain naphthalene. The major constituent of creosote, used for timber impregnation, is naphthalene and its alkyl homologues.
- Nitrogen dioxide: formed by various combinations of oxygen and nitrogen at high temperatures during the combustion process. The higher the combustion temperature, the more nitric oxide is generated. Indeed, 90–95% of the nitrogen oxides are usually emitted as nitric oxide and only 5–10% as nitrogen dioxide, although substantial variations from one source type to another have been observed. In ambient conditions, nitric oxide is rapidly oxidized in air to form nitrogen dioxide by available oxidants (such as oxygen, ozone, and VOCs) and this rapid oxidation velocity is such that it is nitrogen dioxide that is usually considered as a primary pollutant.
- Polycyclic aromatic hydrocarbons: PAHs are widespread environmental pollutants that are formed in the combustion process of carbonaceous materials at high temperature. Indoor air is contaminated by PAHs, which come not only from infiltration or intrusion of outdoor air but also from indoor emission sources such as smoking, cooking, domestic heating with fuel stoves and open fireplaces, as well as incense and candle emissions.
- Radon (Rn): all rocks contain some uranium, typically at concentrations of 1–3 ppm. The uranium content of a soil will be about the same as the uranium content of the rock from which the soil was derived. As radium-226, the immediate parent of radon, is a decay product of uranium, the higher the uranium content of the soil the greater the radium concentration and the higher the chance that houses built on such soil will have high levels of indoor radon. The main source of indoor radon is the radon produced by the decay of radium in the soil subjacent to a house. Soil gas containing radon enters a house through cracks and fractures in the foundations by pressure-driven flow, as the air in a house is generally warmer and therefore at a lower pressure than the subjacent soil gas.
- Trichloroethylene: consumers may be exposed to TCE through the use of wood stains, varnishes, finishes, lubricants, adhesives, typewriter correction fluid, paint removers, and certain cleaners, where TCE is used as a solvent.

Furthermore, some compounds have current evidence uncertain or not sufficient for indoor guidelines (World Health Organization 2010):

- Acetaldehyde
- Asbestos
- Biocides, pesticides
- Flame retardants
- Glycol ethers
- Hexane
- Nitric oxide
- Ozone
- Phthalates
- Styrene
- Toluene
- Xylenes

Asbestos, biocides and pesticides, flame retardants, and phthalates can be classified as EPs. On the other hand, Boor et al. (2017) listed indoor air pollutants in sleep microenvironments as house dust, animal allergens, fungi, bacteria, plasticizers, flame retardants, VOCs (e.g., polyurethane or polyester foam, formaldehyde), and unreacted isocyanates.

#### ***4.1.1 Sampling and Sample Preparation for Indoor Environment***

The indoor environment is just like a concentrator of EPs from various commercial and industrial products (Wang et al. 2016). Then, it needs a correct sampling to achieve the reliable result, taking into account the heterogeneity of the analytical matrix.

We can consider two classes of sampling techniques for indoor air: *active air sampling* and *passive air sampling*. In the first case, we need a pump that is used to force the flow of the air sample through the trap filled with a sorbent material. In the second case, sampling operates without the aid of a pump and consists of a sorbent with a high retention capacity for the target compounds. For EP analysis, active air sampling is more useful and Table 4.2 presents several techniques according to the analyte.

Figures 4.1 and 4.2 show some technologies cited in Table 4.2. Figure 4.3 shows a device based on air sampling pump.

Generally, after the sampling the sample will be forwarded to the laboratory for a chromatographic analysis by GC or LC. For this, the analyte needs to be desorbed from the sorbent material by means of a thermal desorption—commonly used for GC—or using a solvent for solid–liquid extraction for LC.

**Table 4.2** Sampling techniques for EPs in indoor air

Compound	Phase	Sampling technique (active sampling)	Flow rate (L min <sup>-1</sup> )
Nine synthetic musks, four parabens, and one insect repellent	Gaseous	Tenax® TA	0.12
Eight synthetic musks	Gaseous + particulate	PUF + GFF	10
Two synthetic musks, bisphenol A	Gaseous + particulate	PUF + QFF	2
Liner and cyclic siloxanes	Gaseous	Isolute ENV® + SPE cartridge	1.5
Liner and cyclic siloxanes	Gaseous	Tenax® GR/graphitized carbon black	0.12
Bisphenol A	Gaseous + particulate	PUF + QFF	5
Parabens, bisphenol A	Gaseous + particulate	QFF + Amberlite® XAD-2® resin	<13.3
Benzophenone	Gaseous + particulate	PUF + QFF	5
Synthetic musks, bisphenol A, parabens, triclosan	Gaseous + particulate	Amberlite® XAD-2® resin + QMA™ filter	—
Nine synthetic musks	Gaseous	Tenax® TA	100
Liner and cyclic siloxanes	Gaseous + particulate	PUF + QFF	5
Eight synthetic musks	Gaseous	PUF	5
Bisphenol A	Gaseous + particulate	XAD-2 resin + QFF	4
Parabens	Gaseous + particulate	XAD-2 resin/ PUF + QFF	8–9
Parabens	Gaseous + particulate	XAD-2 resin/ PUF + QFF	8–9
Cyclic siloxanes	Gaseous	Isolute ENV® + SPE cartridge	3–6
Liner and cyclic methyl siloxanes	Gaseous	Isolute ENV® + SPE cartridge	0.5
Five synthetic musks	Gaseous	PUF + GFF	—

Adapted from Wang et al. (2016)

PUF Polyurethane foam, QFF quarter fiber filter, GFF glass fiber filter, SPE solid-phase extraction

Particulates (e.g., MP<sub>10</sub>) for metal analysis will be retained under a PVC membrane in a trap cassette (Fig. 4.4) followed by a dissolution and analysis by atomic absorption spectrometry or optical emission spectrometry (Chap. 3).

#### 4.1.2 Methods for EP Analyses in Air

The sample analysis is composed of a sequence of steps illustrated below in Fig. 4.5 for the case of organic EPs.

Table 4.3 describes a compendium of analytical methods dedicated to the EP analysis in indoor air.

**Fig. 4.1** Isolute ENV<sup>®</sup> solid phase for active sampling. Courtesy of Biotage



**Fig. 4.2** Tenax<sup>®</sup> TA porous polymer in a glass tube for active sampling. Courtesy of Sigma-Aldrich

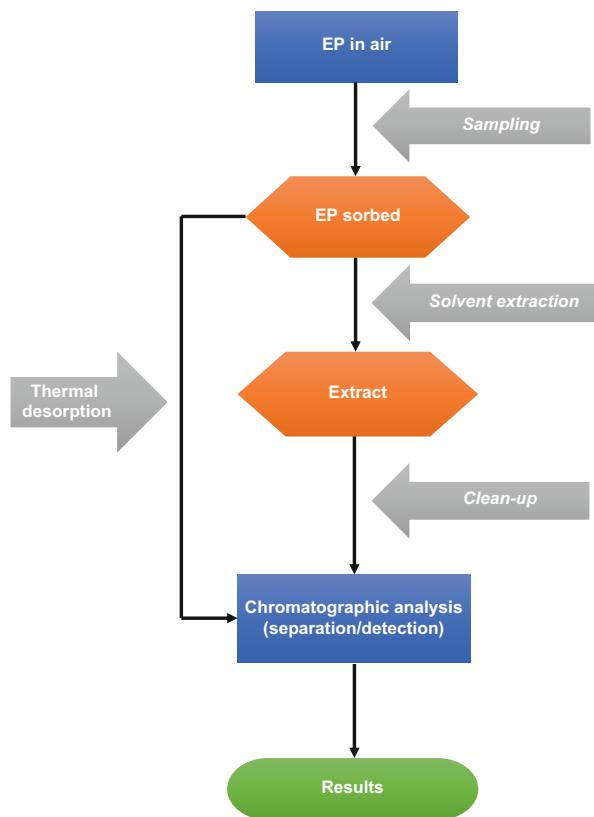
**Fig. 4.3** Air sampling pump. Courtesy of Sigma-Aldrich



**Fig. 4.4** Cassette for particulate sampling.  
Courtesy of Sigma-Aldrich



**Fig. 4.5** The analytical approach for organic EP analysis in air



**Table 4.3** Analytical methods for EP analysis in indoor air

Analyte(s)	Brief method description	LOD	References
VOCs	Method for the determination of VOCs in ambient air using Tenax® adsorption and GC-MS	0.01–100 ppb <sub>v/v</sub>	Method TO-1, U.S. Environmental Protection Agency (1999)
Phenolic compounds	Method for the determination of phenol and methylphenols (creosols) in ambient air using HPLC-UV	1–250 ppb <sub>v/v</sub>	Method TO-8, U.S. Environmental Protection Agency (1999)
Flame retardants (DBE-DBCH, PBT, HBB, DDC-CO, and DBDPE)	Methods for the determination of flame retardants using GC-MS-ECNI	0.41–20 pg m <sup>-3</sup>	Newton et al. (2016)
Polyfluorinated alkyl compounds (nonylphenol, BPA, etc.)	Methods for the determination of polyfluorinated alkyl compounds using GC-MS-PCI, GC-MS-EI/NCI and HPLC-MS	0.15–20 pg m <sup>-3</sup>	Xie and Ebinghaus (2008)

1 ppb v/v = 1 nL of analyte in 1 L of sample. *VOCs* Volatile organic compounds (generally, aromatic compounds as benzene, ethylbenzene, toluene, xylenes, and fluorinated, bromated and chlorinated related compounds with a high vapor pressure), *GC* Gas chromatography, *HPLC* High-performance liquid chromatography, *PCI* Positive chemical ionization, *NCI* Negative chemical ionization, *EI* Electron ionization, *ECNI* Electron capture negative ionization, *UV* Ultraviolet, *DBE-DBCH* Mixture of dimethyl glutarate and dimethyl adipate, *PBT* 10-Hydroxy-10-(2-(2Z)-2-octen-1-ylcyclopropyl)-5,8-decadienoic acid, *HBB* 2-Hydroxybenzylbenzimidazole, *DDC-CO* Dicarbethoxydihydrocollidine, *DBDPE* Decabromodiphenyl oxide

## 4.2 Soil Composition and Properties

Soil is a matrix of the most complex due to the chemical constitution of its organic and inorganic components, and the physical states of the soil—the soil is formed by chemical substances in the solid, liquid, and gaseous states. Then, soils have a natural tendency to interact with different pollutants.

Tables 4.4 and 4.5, and 4.6 present the chemical composition of soil samples of the red latosol type, common in the south-west region in Brazil.

The results presented are typical for red latosol, which were formed under strong weather conditions in hot and humid regions containing low concentrations of silicate minerals and high concentration of FeO, Fe<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>. According to Weber et al. (2005), this type of soil presents variable electric charges on the surface. The largest contents of the sand fraction (Table 4.6) are due to a proximity of the collection points at the river bank. Iron was the natural element determined in higher concentration (Table 4.6). The distribution of organic matter (OM) and the mineral fraction in layers in the soil is as follows:

**Table 4.4** Results of physicochemical analysis of samples of red latosol, collected at different depths

ID	pH CaCl <sub>2</sub>	OM (g dm <sup>-3</sup> )	P resin (mg dm <sup>-3</sup> )	K (mmolc dm <sup>-3</sup> )	Ca (mmolc dm <sup>-3</sup> )	Mg (mmolc dm <sup>-3</sup> )	H <sup>+</sup> + Al <sup>3+</sup> (mmolc dm <sup>-3</sup> )	Al (mmolc dm <sup>-3</sup> )	CTC (mmolc dm <sup>-3</sup> )	S (mmolc dm <sup>-3</sup> )	V (%)	(Ca <sup>+</sup> Mg) K	S <sub>2</sub> SO <sub>4</sub> <sup>2-</sup> (mg dm <sup>-3</sup> )
ST01-0.3m	6	23	5	0.4	45	15	27	—	87	60	69	163	7
ST01-0.6m	5.9	24	43	0.2	35	15	29	—	79	50	63	233	12
ST01-1.4m	6.1	12	3	0.7	47	18	21	—	87	66	76	96	16
ST02-0.3m	4.4	7	0	2.4	6	2	16	8	56	10	19	3	15
ST02-0.6m	4.6	2	0	0.1	7	2	33	10	42	9	21	148	1
ST03-0.3m	5.2	19	3	0.1	11	4	34	2	49	15	31	246	1
ST03-0.6m	5	4	1	0.1	10	3	33	2	46	13	29	213	4
ST04-0.3m	5.5	10	1	1.5	18	6	28	—	54	26	48	16	16
ST04-0.6m	5.6	9	1	1.7	22	7	27	—	57	31	54	17	23
ST05-0.3m	6.1	19	2	0.6	30	10	22	—	62	41	65	67	1
ST05-0.6m	5.7	5	1	0.1	21	8	21	—	50	29	58	210	21
ST06-0.3m	5.6	15	0.8	0.8	22	9	34	—	66	32	48	41	88
ST06-0.6m	4.3	16	1.2	5	1	95	18	102	7	7	5	139	
ST07-0.3m	5.4	30	35	1.1	22	7	36	1	66	30	46	25	9
ST07-0.6m	5.8	25	8	1	42	15	25	—	83	58	70	58	8
ST08-0.3m	6	27	63	1.2	60	22	22	—	106	83	79	67	7
ST08-0.6m	6	30	39	1.1	58	19	24	—	102	78	76	68	8

OM Organic matter, CEC Cation-exchange capacity, S Sum of bases saturated with Na, V Saturation of bases Analyses carried out according to methods from the Brazilian Agricultural Research Corporation (1997)

**Table 4.5** Results of granulometric analysis ( $\text{g kg}^{-1}$ ) of red latosol samples, collected at different depths

ID	Sand	Clay	Silt
ST01-0.3m	655	282	63
ST01-0.6m	641	278	81
ST01-1.4m	661	247	92
ST02-0.3m	662	230	108
ST02-0.6m	267	555	178
ST03-0.3m	235	560	205
ST03-0.6m	398	276	326
ST04-0.3m	404	192	404
ST04-0.6m	289	463	248
ST05-0.3m	377	270	353
ST05-0.6m	369	140	491
ST06-0.3m	202	559	239
ST06-0.6m	187	609	204
ST07-0.3m	289	442	269
ST07-0.6m	405	359	236
ST08-0.3m	233	578	189
ST08-0.6m	260	511	229

Analyses carried out according to methods from the Brazilian Agricultural Research Corporation (1997)

**Table 4.6** Results of analysis of chemical elements ( $\text{mg kg}^{-1}$ ) in samples of red latosol, collected at different depths

ID	B	Cu	Fe	Mn	Zn
ST01-0.3m	10.8	6.2	28	33	2.4
ST01-0.6m	11.5	4.6	44	34.2	1.7
ST01-1.4m	11.6	5.3	30	18.9	3.5
ST02-0.3m	3.7	6.9	56	8.5	1.2
ST02-0.6m	0.2	2.2	6	6	1.7
ST03-0.3m	4.4	6.3	64	37.1	1.8
ST03-0.6m	1.8	4.2	29	4.7	0.5
ST04-0.3m	1.1	3.7	8	9.3	0.3
ST04-0.6m	0.4	2.5	5	3.6	0.3
ST05-0.3m	3.5	5.4	24	25.4	3.2
ST05-0.6m	5.3	2.5	9	1.3	0.3
ST06-0.3m	11.6	3.7	22	1.7	1.1
ST06-0.6m	11.6	3.5	19	19.5	1.8
ST07-0.3m	1.1	2.9	24	32.7	2.2
ST07-0.6m	1.8	4.3	18	26.3	6.4
ST08-0.3m	1.6	4.9	32	32	4.4
ST08-0.6m	1.9	3.1	31	34.5	3.6

Analyses carried out according to methods from the Brazilian Agricultural Research Corporation (1997)

- Horizon O (surface): OM in decomposition (0.3 m of depth)
- Horizon A: OM accumulated mixed with the mineral fraction (0.6 m of depth)
- Horizon B: clay accumulation,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , and low OM content (approximately 1 m of depth)
- Horizon C: materials from rock mother

Thus, it is expected that the higher the concentration of OM, especially of humic acids present in it, the greater the retention capacity of metallic cations in soils, especially in Horizon O, which leads to a reduction in the transport of metallic pollutants in the soil, as the humic substances act as strong complexing agents due to the presence of binding sites formed by carboxylic and phenolic groups (Clapp et al. 2001). Therefore, a higher concentration, for example, of bivalent metal cations in the samples of Horizons O and A of the soil is expected, considering the effect of the presence of silicate compounds in the metal retention, where a greater cation-exchange capacity (CEC) of the soil denotes a higher availability of binding sites for the metal after the exit of cations or protons associated with these silicates, due to the negative surface charge of the latter.

Figure 4.6 shows a soil with a high content of clay.

**Fig. 4.6** Soil with a high content of clay



According to the University of the West of England (2013), the main pollutants observed in European soil are:

- Asbestos
- Dioxin and dioxin-like chemicals
- Metals: cadmium, lead, mercury
- Nonmetal: arsenic
- Persistent organic pollutants (POP): polychlorinated biphenyls (PCBs), polybrominated biphenyls, polychlorinated dibenzofurans (PCDFs), polycyclic aromatic hydrocarbons (PAHs), organophosphorus and carbamate insecticides (pesticides), herbicides, organic fuels (gasoline, diesel), and pharmaceuticals and their metabolites

#### ***4.2.1 Sampling and Sample Preparation***

Soil samples are collected using the following procedure (U.S. Environmental Protection Agency 1997):

- (a) Carefully remove the top layer of soil to the desired sample depth with a precleaned spade.
- (b) Using a precleaned, stainless steel scoop, spoon, trowel, or plastic spoon, remove and discard the thin layer of soil from the area that came into contact with the shovel.
- (c) Transfer the sample into an appropriate container using a stainless steel or plastic lab spoon or equivalent. If composite samples are to be collected, place the soil sample in a stainless steel or plastic bucket and mix thoroughly to obtain a homogeneous sample representative of the entire sampling interval. Place the soil samples into labeled containers. [Caution: Never composite volatile organic analysis (VOA) samples.]
- (d) VOA samples should be collected directly from the bottom of the hole before mixing the sample to minimize volatilization of contaminants.
- (e) Check to ensure that the VOA vial Teflon liner is present in the cap, if required. Fill the VOA vial fully to the top to reduce headspace. Secure the cap tightly. The chemical preservation of solids is generally not recommended. Refrigeration is usually the best approach, supplemented by a minimal holding time.
- (f) Ensure that a sufficient sample size has been collected for the desired analysis, as specified in the sampling plan<sup>1</sup>.

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<sup>1</sup>A plan containing, basically, amount of samples, location, methods, QA/QC, and logistic of sampling. Steps related to the sample plan are (National Institute of Standards and Technology 2017) the following: (1) identify the parameters to be measured, the range of possible values, and the required resolution; (2) design a sampling scheme that details how and when samples will be taken; (3) select sample sizes; (4) design data storage formats; and (5) assign roles and responsibilities.

- (g) Decontaminate equipment between samples.
- (h) Fill in the hole and replace grass turf, if necessary.

After the sampling, samples should obey the follow requirements:

- Holding time: 14 days from sampled
- Minimum volume: 100 g
- Container type: two 40 mL vials and no air space (for volatile compounds); glass jar with Teflon-lined cap (for other compounds)
- Preservation: cool to 4 °C (ice in cooler)

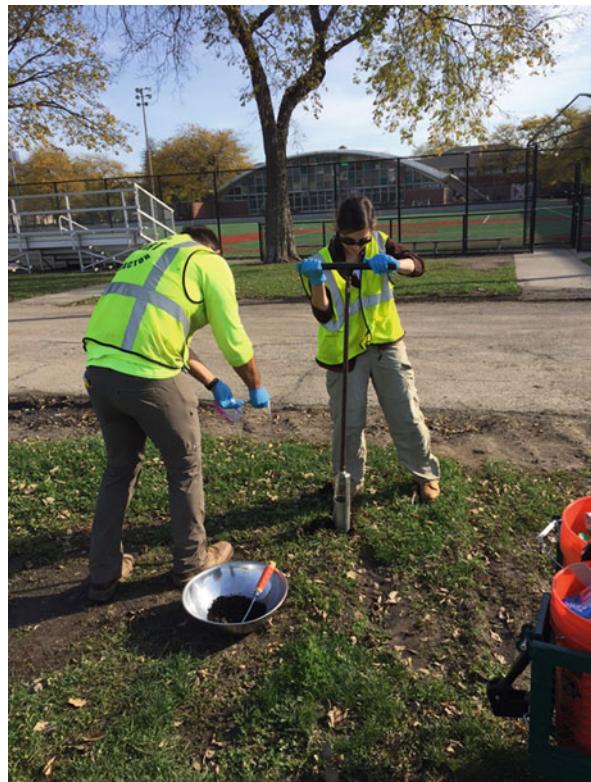
The sample preparation for the analysis step comprises:

- (a) Extraction by means solvent (solid–liquid, Soxhlet, accelerated solvent extraction, etc.), according to the analyte and matrix physicochemical properties.
- (b) Cleanup by means of the use of solid-phase extraction (SPE) or another technique (see Chap. 3).
- (c) Injection for the chromatographic analysis.

For analysis of metals, samples need a digestion in mineral acid, as nitric acidic, or a microwave-assisted digestion.

Figure 4.7 shows a soil sampling.

**Fig. 4.7** Soil sampling with an auger device. Courtesy of U.S. EPA



### 4.2.2 Methods for EP Analyses in Soil

Table 4.7 describes a compendium of analytical methods dedicated to the EP analyses in soil.

## 4.3 Water Composition and Properties

When we talk about water as an environmental matrix, we must consider it in the plural, since we are dealing with two distinct types, the *surface water* and the *groundwater*. The surface water is that found in rivers, lakes, seas, and oceans, while groundwater is that found in the aquifers. Drinking water and wastewater are classifications related to surface and groundwater according to their use. Table 4.8 shows the main characteristics of each of them.

A variation in the water composition is expected according to climate and environmental conditions.

It may be noted that for most of the ions listed in the Table 4.8 there is an increase in their concentration when considering groundwater relative to surface water (except for  $\text{Cl}^-$  ion). As observed by Snoeyink and Jenkins (1996), groundwater, which has a higher concentration of  $\text{CO}_2$  gas, is in greater contact with rocks and soil, which leads to a longer dissolution time. The carbonic acid ( $\text{H}_2\text{CO}_3$ ) produced by the solubilization of  $\text{CO}_2$  when in contact with these materials leads to the solubilization of the minerals, releasing their constituent ions.

A large amount of suspended material can be found mainly in surface waters. Clay, sand, and organic matter are examples of particles in suspension. There is also a large amount of microorganisms present in water, highlighting bacteria such as

**Table 4.7** Analytical methods for analyses of EPs in soils

Analyte(s)	Brief method description	LOD	References
Alprostadil (vasodilator) and ethinyl estradiol (semisynthetic alkylated estradiol)	Methods for the determination of steroid estro- gen using GC-MS	300–570 ng g <sup>-1</sup>	Gunatilake et al. (2016)
Melamine (used in the manufacture of plastics, flame retardants, coatings, and other products)	Method for the determination of melamine using HPLC-DAD	0.01 mg kg <sup>-1</sup>	Nong et al. (2014)
Antibiotics (sulfadiazine, roxithromycin)	Method for the determination of antibiotics using LC-MS-MS	–	Sun et al. (2015)
Antibiotic (OTC)	Method for the determination of OTC antibiotic in soils using HPLC-UV	<1 mg L <sup>-1</sup>	Vaz Jr. (2016)

*GC* Gas chromatography, *HPLC* High-performance liquid chromatography, *LC* Liquid chromatography, *MS* Mass spectrometry, *DAD* Diode array detector, *UV* Ultraviolet

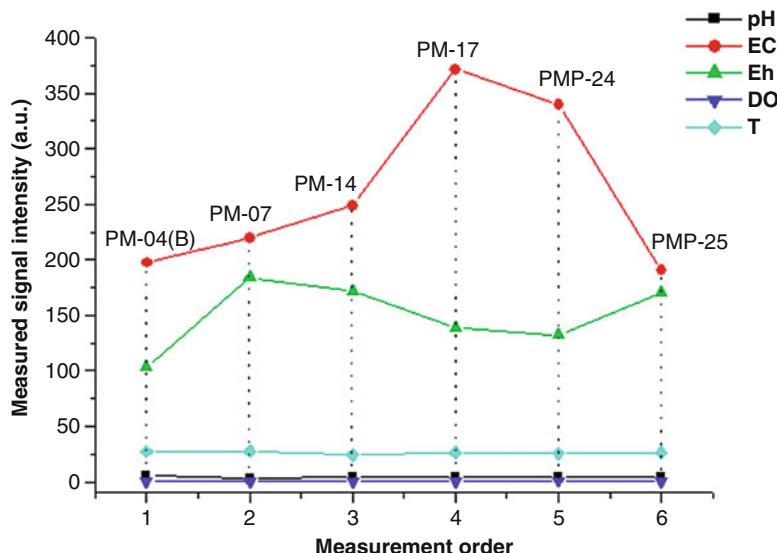
**Table 4.8** Typical surface water and groundwater composition in the United States, according to Snoeyink and Jenkins (1996)

Chemical species	Concentration in surface water (mg L <sup>-1</sup> )	Concentration in groundwater (mg L <sup>-1</sup> )
SiO <sub>2</sub>	1.2	10
Fe <sup>3+</sup>	0.02	0.09
Ca <sup>2+</sup>	36	92
Mg <sup>2+</sup>	8.1	34
Na <sup>+</sup>	6.5	8.2
K <sup>+</sup>	1.2	1.4
HCO <sub>3</sub> <sup>-</sup>	119	339
SO <sub>4</sub> <sup>2-</sup>	22	84
Cl <sup>-</sup>	13	9.6
NO <sub>3</sub> <sup>-</sup>	0.1	13
Total dissolved solids	165	434
Total hardness as CaCO <sub>3</sub>	123	369

coliforms and cyanobacteria, which often compromise the quality of water, especially surface water.

Important analytical parameters for the monitoring of water quality are the following:

- Electrical conductivity (EC): It provides information on the distribution of ionic species in the medium, with the conductivity being directly proportional to the concentration of these species.
- Dissolved oxygen (DO): O<sub>2</sub> gas has a low solubility in water, with a reduction of its concentration indicating its consumption by the chemical oxygen demand (COD) for the formation of oxidized species, as well as consumption by biochemical demand (BOD) due to the activity of the metabolism of present micro-organisms—groundwater has DO values much smaller than surface waters.
- pH: Its value indicates the concentration of H<sup>+</sup> in the medium—a pH value around 6 is the most common in drinking waters; however, there are variations due to the presence of organic or inorganic species.
- Redox potential (E<sub>h</sub>): It indicates the oxidizing or reducing characteristic of the medium, having a direct correlation with the pH values.
- Presence of organic compounds: Determination of petroleum derivatives, agrochemicals, and organochlorine compounds produced by treatment processes, which are the main *xenobiotics* observed in waters, among others, as the EPs.
- Presence of toxic metals: Cadmium, mercury, chromium, etc., are also, in most cases, xenobiotic species.



**Fig. 4.8** Behavior of physicochemical parameters measured in situ with the use of multiparameter probe in groundwater located in the southeast region of Brazil. PM Monitoring well, PMP Deep monitoring well. EC in  $\mu\text{S m}^{-1}$ ,  $E_h$  in mV, DO in  $\text{mg L}^{-1}$ , and T in  $^{\circ}\text{C}$

Figure 4.8 shows an example of in situ measurements for the physicochemical parameters mentioned above. We can observe that EC and  $E_h$  presented the main variation in their values, probably due to the variability in the concentration of ionic species presented in each monitoring well.

Figure 4.9 shows a water body (surface water) that can also be monitored using the analytical parameters in Fig. 4.8.

Unfortunately, water bodies—especially surface water—are the main route of exposition to EPs due to the fact that these bodies receive a large amount of pharmaceuticals and healthcare products from the human use and excretion.

Other water-related matrices are the following:

- Sediments: naturally occurring material, as rocks, sand, and silt, in contact with water bodies, as rivers
- Sewage or municipal wastewater
- Sludge: a residual semisolid material from industrial, water, or wastewater treatment processes
- Wastewater: result of a domestic, industrial, commercial, or agricultural activities, with negative impacts to the human health and environment

**Fig. 4.9** Small creek  
(surface water)



The World Health Organization (2017) established the occurrence of chemicals in drinking waters (Table 4.9).

#### **4.3.1 Sampling and Sample Preparation**

The sampling of surface water takes into account the following (U.S. Environmental Protection Agency 2016):

- (a) Surface water samples will typically be collected either by directly filling the container from the surface water body being sampled or by decanting the water from a collection device such as a stainless steel scoop or other device.
- (b) During sample collection, if transferring the sample from a collection device, make sure that the device does not come in contact with the sample containers.

**Table 4.9** Categorization of sources of chemicals in drinking water, according to the World Health Organization (2017)

Source	Examples
Naturally occurring chemicals (including naturally occurring algal toxins)	Rocks and soils (e.g., calcium, magnesium but also arsenic and fluoride, cyanobacteria in surface water)
Chemicals from agricultural activities (including pesticides)	Application of manure, fertilizer, and pesticides; intensive animal practices
Chemicals from human settlements (including those used for public health purposes, e.g., vector control)	Sewage and waste disposal, urban runoff, fuel leakage
Chemicals from industrial activities	Manufacturing, processing, and mining
Chemicals from water treatment and distribution	Water treatment chemicals; corrosion of and leaching from storage tanks and pipes, by-products of chemical treatment

- (c) Place the sample into appropriate, labeled containers. Samples collected for volatile organic compounds (VOCs) analysis must not have any headspace. All other sample containers must be filled with an allowance for ullage.
- (d) All samples requiring preservation must be preserved as soon as practically possible, ideally immediately at the time of sample collection. If preserved VOC vials are used, these will be preserved with concentrated hydrochloric acid prior to departure for the field investigation. For all other chemical preservatives, use the appropriate chemical preservative generally stored in an individual single-use vial. The adequacy of sample preservation will be checked after the addition of the preservative for all samples, except for the samples collected for VOC analysis. If it is determined that a sample is not adequately preserved, additional preservative should be added to achieve adequate preservation.
- (e) All samples preserved using a pH adjustment (except VOCs) must be checked, using pH strips, to ensure that they were adequately preserved. This is done by pouring a small volume of sample over the strip. Do not place the strip in the sample. Samples requiring reduced temperature storage should be placed on ice immediately.

These recommendations can be extended to wastewater and sewage.

For groundwater, sampling recommendation comprises the following (U.S. Environmental Protection Agency 2013):

- (a) Groundwater samples will typically be collected from the discharge line of a pump or from a bailer, either from the pour stream of an upturned bailer or from the stream from a bottom-emptying device. Efforts should be made to reduce the flow from either the pump discharge line or the bailer during sample collection to minimize sample agitation.
- (b) During sample collection, make sure that the pump discharge line or the bailer does not contact the sample container.

- (c) Place the sample into appropriate labeled containers. Samples collected for VOC, acidity, and alkalinity analysis must not have any headspace. All other sample containers must be filled with an allowance for ullage.
- (d) All samples requiring preservation must be preserved as soon as practically possible, ideally immediately at the time of sample collection. If preserved VOC vials are used, these will be preserved with concentrated hydrochloric acid prior to departure for the field investigation. For all other chemical preservatives, use the appropriate chemical preservative generally stored in an individual single-use vial. The adequacy of sample preservation will be checked after the addition of the preservative for all samples except for the samples collected for VOC analysis. If additional preservative is needed, it should be added to achieve adequate preservation.

Furthermore, according to the U.S. Environmental Protection Agency (2013) special sample-handling procedures should be instituted when trace pollutant samples are being collected. All sampling equipment, including pumps, bailers, water-level and measurement equipment, which come into contact with the water in the well must be cleaned in accordance with cleaning procedures. Pumps should not be used for sampling unless the interior and exterior portions of the pump and the discharge hoses are thoroughly cleaned. Blank samples should be collected to determine the adequacy of cleaning prior to collection of any sample using a pump other than a peristaltic pump.

For organic EPs, the best preservation method is cool to 4 °C, and add sulfuric acid to pH value below 2, using a glass container. The holding time is 28 days.

In the case of metals, generally filter samples on-site, and add nitric acid to pH value below 2, using a glass or plastic container. The holding time is 6 months.

After the sampling, samples will pass by the following steps:

- (a) Analyte extraction, using liquid–liquid extraction with a solvent, solid-phase extraction (SPE), or solid-phase microextraction (SPME).
- (b) Cleanup before the extract injection in the chromatographic system, by means of a SPE.

Figure 4.10 shows a surface water sampling.

### 4.3.2 *Methods for EP Analyses in Water*

Table 4.10 describes a compendium of analytical methods dedicated to the EP analysis in water.



**Fig. 4.10** Surface water sampling in a lagoon. Courtesy of U.S. EPA

#### 4.4 Conclusions

Air, soil, and water have a heterogenic chemical composition, which promotes a large variation in their properties, functionality, and interaction with pollutants.

Nowadays, there is a large variety of technologies of sampling and analysis available for environmental analytical laboratories, which can reduce significantly the time consumed to generate the analytical result.

Despite the availability of advanced techniques as separation and detection, sampling and sample preparation are steps that require attention for the analyses of EPs in environmental matrices. The right choice of both methods will lead to the efficiency of the analytical approach applied.

**Table 4.10** Analytical methods for EP analysis in water

Analyte (s)	Brief method description	LOD	References
Pharmaceuticals (naproxen, ketoprofen, diclofenac, ibuprofen, mefenamic acid), perfluorinated compounds (PFOA, PFOS) and caffeine	Method for the determination of pharmaceuticals, perfluorinated compounds, and caffeine by LC-MS/MS	0.15 ng mL <sup>-1</sup>	Magi et al. (2018)
Polar pesticides (atrazine, carbendazim, desethylatrazine, desethylterbutylazine, diuron, S-metolachlor, terbutylazine; pharmaceuticals (alprazolam, atenolol, carbamazepine, diazepam, diclofenac, ibuprofen, naproxen); steroid hormones (17- $\alpha$ -estradiol, 17- $\alpha$ -ethinylestradiol, 17- $\beta$ -estradiol, estriol, estrone); brominated diphenyl ethers (BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154); fluorinated surfactants (PFOA, PFOS); bisphenol A; triclosan	Method for the determination of polar pesticides, pharmaceuticals, steroid hormones, brominated diphenyl ethers, fluorinated surfactants, bisphenol A, and triclosan by LC-MS (ESI)	0.3–75 ng L <sup>-1</sup>	Vrana et al. (2016)
Phthalate esters (bis(2- <i>n</i> -butoxyethyl) phthalate, bis(2-ethoxyethyl) phthalate, bis(2-methoxyethyl) phthalate, bis(4-methyl-2-pentyl) phthalate, diethyl phthalate, dicyclohexyl phthalate, dihexyl phthalate, diisobutyl phthalate, dinonyl phthalate, hexyl 2-ethylhexyl phthalate)	Method for the determination of phthalate esters by GC-ECD	22–640 ng L <sup>-1</sup>	U.S. Environmental Protection (1996)
Multiclass pharmaceuticals (analgesics/anti-inflammatories, antibiotics, lipid regulators, $\beta$ -blockers, antiepileptic/psychiatrics ulcer healings, diuretics, hormones and bronchodilators), lifestyle products (caffeine, nicotine), drugs of abuse and their metabolites, pesticides and some of their more relevant metabolites, nitrosamines, flame retardants, plasticizers, and perfluorinated compounds	Multi-residue method of determination of over 400 priority and emerging pollutants by rapid-resolution LC-TOFMS	<10 ng L <sup>-1</sup>	Robles-Molina et al. (2014)

(continued)

**Table 4.10** (continued)

Analyte (s)	Brief method description	LOD	References
Pharmaceuticals (carbamazepine, ofloxacin, and piroxicam)	Method for the determination of carbamazepine, ofloxacin, and piroxicam in waters using excitation–emission photoinduced fluorescence data and multivariate calibration, without the necessity of chromatographic separation	2–7 ng mL <sup>-1</sup>	del Carmen Hurtado-Sánchez et al. (2015)
Pharmaceuticals (ibuprofen, diclofenac, bezafibrate, ketoprofen, and mefenamic acid)	Method for screening of pharmaceuticals in waters by means of CE-C <sup>4</sup> D	0.20–0.81 mg L <sup>-1</sup>	Le et al. (2016)

*GC* Gas chromatography, *HPLC* High-performance liquid chromatography, *LC* Liquid chromatography, *ECD* Electron capture detector, *MS* Mass spectrometry, *TOFMS* Time-of-flight mass spectrometry, *ESI* Electrospray ionization, *PFOA* Pentadecafluorooctanoic acid, *PFOS* Perfluorooctanesulfonic acid, *CE* Capillary electrophoresis, *C<sup>4</sup>D* Coupled contactless conductivity detection

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