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Chemical migration in drinking water stored in polyethylene terephthalate (PET) bottles: a source of controversy.

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Abstract:

Due to its chemical inertness and physical properties PET is particularly suitable for food packaging applications, especially for drinking water. More bottled water is consumed than other bottled beverages. This article is a survey and toxicological investigation of chemical compounds, which are able to diffuse from PET bottles to water. The exact detailed chemical composition of plastic materials is known only from information provided by manufacturers. A declaration of conformity according to EC regulation no.10/2011 is required to ensure the safety of plastic materials in contact with foodstuffs. This regulation established a positive list of monomers and additives which are authorized for use in plastic materials. Some substances are subject to restrictions and/or specifications according to their toxicological data. However, Non-Intentionally Added Substances (NIAS) not listed in this regulation such as breakdown products from monomers and additives and/or impurities found in initial polymerization reactants may be present in a PET bottle wall. Also, recycled PET can be a source of unknown chemical compounds found in water. All these substances may potentially migrate from the PET bottle wall to bottled water.

It is well-known that acetaldehyde and antimony are leached from PET bottles. However, several studies have shown the presence of other substances not expected *a priori* in bottled water, sometimes in non-negligible concentrations. The origin of these compounds has not been clearly established and remains controversial (PET container, cap sealing resins, background contamination, water processing steps, NIAS, etc). Overall, it is difficult to compare the reported results due to the variety of parameters favoring the release of substances (contact time, type of simulant, temperature, sunlight exposure and bottle color). Considering all these difficulties and controversies, further investigations are needed to clearly identify the migration products from PET and to ensure that the consumption of PET-bottled water does not involve any health hazards.

Keywords:

Bottled water, migration, acetaldehyde, mutagenicity, genotoxicity, endocrine disruptors.

List of abbreviations:

Ag: Silver

Al: Aluminum

APEOs: Polyethoxylated nonylphenols

As: Arsenic

Ba: Barium

BBP: Benzylbutyl phthalate

BHET: Bis(hydroxyethyl) terephthalate

BHT: Butylated hydroxytoluene

BPA: Bisphenol A

Ce: Cesium

Cd: Cadmium

Co: Cobalt

Cr: Chromium

Cu: Copper

DBP: Dibutyl phthalate

DiBP: Di-iso-butyl phthalate

DEHP, Di-2-(ethylhexyl) phthalate

DEHA: Bis-2-ethylhexyl adipate

DEP: Diethyl phthalate

DMSO: Dimethyl sulfoxide

DOP: Di-n-octyl phthalate

EEC: European Economic Community

EEQs: Estradiol equivalents

Fe: Iron

GC-MS: Gas chromatography – Mass spectrometry

Ge: Germanium

HDPE: High density polyethylene

HULYs: Human blood lymphocytes

LDH: Lactate dehydrogenase

Mg: Magnesium
Mn: Manganese
Mo: Molybdenum
MTT: 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide
NIAS: Non-intentionally added substances
Ni: Nickel
NP: 4-Nonylphenol
OP: Octylphenol
PA: Polyamide
Pb: Lead
PC: Polycarbonate
PET: Polyethylene terephthalate
PhA: Phthalic acid
PVC: Polyvinylchloride
Sb: Antimony
Sb₂O₃: Antimony trioxide
Se: Selenium
SEC-HPLC: Size exclusion chromatography – High performance liquid chromatography
SML: Specific migration limits
SPE: Solid-phase extraction
SPME: Solid-phase micro-extraction
SODIS: Solar water disinfection
RPE: Relative proliferative effects
TDI: Tolerable daily intake
TNPP: Tris(nonylphenyl) phosphite
TOC: Total Organic Carbon
Ti: Titanium
YES: Yeast estrogen screen
Zn: Zinc
Zr: Zirconium

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1. Introduction.

The consumption of bottled water is very widespread. For example, more than 53 000 m³ were drunk in Europe in 2004, which was the biggest annual consumption thus far (Gleick et al., 2006). Polyethylene terephthalate (PET) is a semi-crystalline polymer belonging to the family of polyesters. It is the most widespread polymer used for the manufacture of food contact packaging and films, especially for beverages and drinking water. PET bottles for drinking water have been marketed for the last four decades and were introduced to the French market at the beginning of the 1980's. PET bottles have gradually replaced polyvinyl chloride (PVC) and glass bottles in markets. The use of this material has enabled the manufacture of light, unbreakable and highly transparent containers (ILSI, 2000).

During this time, numerous studies have investigated the interaction of PET bottles in contact with drinking water. These studies focused on the release of PET initial reactants (monomers and catalysts), reaction by-products and plastic additives into bottled water. The monitoring of several substances by migration-controlled processes that simulate actual storage conditions with respect to time, temperature, and sunlight exposure has also been widely reported (Franz et al., 2004; Widén et al., 2004; Feigenbaum et al., 2005; Vitrac et al., 2007; Welle and Franz, 2008; Franz and Welle, 2009a).

Furthermore, the potential toxicity of bottled water packed in PET has also been investigated. Several authors have reported finding chemical mixtures with estrogenic activity in PET-bottled water. The presence of NIAS has been suggested as the source of this toxicological effect (Evandri et al., 2000; Leivadara et al., 2008). Although compounds used for the manufacture of plastic packaging are carefully controlled, the stressing of material during their production can change the chemical structures and generate degradation products, which may have an estrogenic activity (Yang et al., 2011).

A review of the literature shows that contradictory results for PET-bottled water have been reported concerning the presence of chemical compounds and hazard assessments. These differences could be explained by the large variety of analytical methods, bioassays and exposure conditions involved. Furthermore, in some cases, the origin of substances found in bottled drinking water was not clearly established and remains to be elucidated. For the moment, the safety of PET bottles for drinking water is still in question.

1.1 Polyethylene terephthalate (PET) used for drinking water bottles.

1.1.1 The synthesis of PET.

The prepolymerization of dimethylterephthalate or terephthalic acid with ethylene glycol is the first industrial step in the synthesis of PET. Both reactions generate low weight oligomers and an intermediate compound named bis(hydroxyethyl)terephthalate (BHET). After this step, a second polycondensation is carried out with an antimony (Sb), germanium (Ge), titanium (Ti), cobalt (Co), magnesium (Mg) or zinc (Zn) based catalyst (ILSI, 2000; Fakirov, 2002). During PET manufacturing, several degradation and decomposition reactions can be produced (Zimmerman, 1977; McNeill and Bounekhel, 1991; Montaudo et al., 1993). Romão et al., (2009b) reviewed the degradation mechanisms and secondary reactions on PET synthesis. Temperature and oxygen in the PET melt process can promote thermo-mechanical and thermo-oxidative reactions. Sub-products such as acetaldehyde, oligomers and diethylene glycol may be generated and they are potential migrants presents in PET raw material (Besnoin and Choi, 1989).

Hydrolysis is a degradation reaction of PET which can occur due to the presence of water during the melt process (Zhang and Ward, 1995; Paci and La Mantia, 1998). Every chain scission produces carboxyl and alcohol end groups (Campanelli et al., 1993).

PET thermal degradation generates volatile organic compounds. Carbon monoxide, aldehydes (formaldehyde, acetaldehyde, benzaldehyde), C₁-C₄ aliphatic hydrocarbons, aromatic hydrocarbons (benzene, toluene, ethylbenzene and styrene), esters (vinyl benzene, methyl acetate), methanol, acetophenone and 2-methyl-1,3-dioxolane were identified in PET samples submitted to temperatures between 200 and 300°C (Dzięcioł and Trzeszczyński, 2000). Franz and Welle (2008) reported 1,3-dioxolane and 2-methyl-1,3-dioxolane as thermal degradation products in PET bottles.

However, Holland and Hay (2002b) have shown that PET thermal stability depends on the type of co-monomers used for its production. Concerning bottle-grade PET, a co-polymerization with diethylene glycol and isophthalic acid is usually done to minimize polymer thermal crystallization during production of preforms and the blow-molding process. Both co-monomers reduce the size of spherulites and as a result, the final container is transparent (Holland and Hay, 2002a). Indeed, glass-like transparency is a valued commodity for drinking-water bottles. Also, the crystallization rate has a direct effect on the barrier properties of PET. Gas permeability and the diffusion rate are directly affected by the degree of crystallinity and the orientation of PET films and bottles (Awaja and Pavel, 2005; Tadmor and Gogos, 2006; Romão et al., 2009a).

1.1.2 The manufacture of PET bottles for drinking water.

In the packaging industry, bottles and containers can be produced by different techniques. Injection blow molding is the preferred process for manufacturing PET bottles. Amorphous preforms are obtained by processing PET granules. Preforms are stretched by a blow molding process to achieve biaxially oriented bottles (ILSI, 2000; Pennarun, 2001; Awaja and Pavel, 2005).

The barrier properties of PET bottles are the combined result of higher deformation-induced crystallization (25 % for carbonated beverage bottles) and orientation. The selection of an

adequate blow temperature around 20°C above the PET glass transition temperature (T_g) is essential to achieve these properties (Tadmor and Gogos, 2006).

Additives such as plasticizers and antioxidants are not necessary for PET bottles and colorants are added in small quantities. Copper phthalocyanine blue is used as a pigment for food contact packaging. Benzotriazole UV stabilizers are added in PET to protect some kinds of food from light. For example, Tinuvin 326 is added into bottle grade PET to protect edible oil against photo-oxidation. Also, acetaldehyde scavengers are used in PET bottles for mineral water (Ashby, 1988; ILSI, 2000; Coltro et al. 2003; FSA, 2007). Villain et al., (1995) have tested various stabilizers to minimize the generation of acetaldehyde and formaldehyde by thermal degradation of PET during the injection molding of preforms. A method for the manufacturing of PET bottles with acetaldehyde scavengers was designed and patented by Jen (2002). Furthermore, it is generally known that antioxidants with hindered phenol containing calcium and a phosphorus stabilizer are used to produce PET resins. Hexanedioic acid polymer with 1,3-benzenedimethanamine is another acetaldehyde scavenger used in PET bottles made of a sheet of polyamide (PA) between two PET layers (multi-layer structure). The addition of this scavenger inhibits the yellowing of the polymer caused by the chemical reaction of PA with acetaldehyde. However, the interaction of PET with this scavenger could produce degradation products such as hexanedioic acid and 1,3-benzenedimethamine monomers, oligomers and breakdown products similar to the degradation of PA (FSA, 2007). The PA layers can also generate NIASs as shown by Franz and Welle (2008).

Nowadays, the recycling of PET bottles is a common environmentally-friendly procedure, used to reduce plastic waste and to reprocess the material for other applications. It is assumed that plastic packaging waste could contain residual contaminants from previous use (storage of detergents, pesticides, fuel...etc.) and that these substances may represent a health risk (Demertzis et al. 1997, Awaja and Pavel, 2007). Decontamination of PET is an important step

for eliminating the presence of unknown compounds in the polymeric material. In Europe, EC Regulation no. 282/2008 has set guidelines for the recycling of plastics for food contact applications. A variety of recycling technologies has been developed for plastic packaging. Awaja and Pavel (2005) have reviewed the PET recycling process for industrial applications.

1.2 European regulations for plastic food contact materials.

The characteristics of plastic materials intended to come into contact with food are governed by the Framework European Regulation no.1935/2004 (EU, 2004). This regulation covers 17 groups of different materials. It states that food contact material should not transfer its constituents to food in quantities that could incur a human health risk, cause an unacceptable change in the composition of the food or bring about deterioration in the organoleptic characteristics of the food. Regulation no.1935/2004 is complemented with specific measures depending on the type of material. Food contact plastic materials are covered by the recent regulation no 10/2011 (EU, 2011) published in January in the Official Journal of the European Community and which repeals directives 2002/72/EC, 80/766/EEC and 81/432/EEC. This new regulation applies to materials and articles made solely of plastic and it has been extended to include plastic layers in multi-material, multi-layers products. It establishes authorized monomers and additives in the plastic formulation on a positive list. The conformity of a plastic material to come in contact with food is based on migration tests. The overall migration limit should not exceed 10 mg of the total constituents released for dm^2 of packaging surface. A specific migration limit (SML), established according to the toxicological data is provided for some substances on the positive list. The principal limitation of this regulation concerns impurities and breakdown products generated by authorized initial reactants and additives (NIASs). Furthermore, the new regulation specifies: “the notion of the risk due to the substance concerns the substance itself, the impurities of this substance and any reaction or degradation products”.

The main aim of this article is to provide a compilation of all known and still controversial data about substances which have been found in PET-bottled drinking water. The experimental migration conditions, the toxicological approaches and the source of water pollution will be discussed in order to clarify the relevance of PET packaging as a source of the migration of chemical compounds into bottled drinking water.

2. Substances investigated in PET and PET-bottled water.

2.1 PET monomers and oligomers.

Several authors have reported residual reactants and low molecular weight breakdown products in PET bottles as potential migrants. Concerning the presence of monomers and residual reactants in the polymer, Begley et al. (2004) quantified terephthalic acid (6.9 mg/L), monohydroxy ethylene terephthalic acid (34.4 mg/L), BHET (49.1 mg/L) and cyclic trimer (9592 mg/L) in commercial beverage PET bottles. Ethylene glycol and terephthalic acid were also identified by Kim et al. (1990) in amber PET bottles for pharmaceutical uses.

Several authors have identified oligomers in PET bottles used for mineral water and foods (Barnes et al., 1995; Monteiro et al., 1998; Nasser et al., 2005). In PET bottles graded for mineral water, Mutsuga et al. (2005) reported levels of oligomers ranging from 4.9 to 8.7 mg/g.

There is a lack of studies of monomer migration from PET to bottled water. Morelli-Cardoso et al. (1997) carried out ethylene glycol migration experiments in 16 virgin PET bottles coming directly from the Brazil packaging industry. The bottles were filled with distilled water, 3% of aqueous acetic acid and 15% of aqueous ethanol. For all cases, ethylene glycol migration was detected after 10 days at 40°C. In contrast, Monarca et al. (1994) detected terephthalic acid and dimethyl terephthalate in distilled water contained in PET bottles stored under the same conditions.

A review of the literature did not turn up any other studies of diffusion into PET-bottled water. Food simulants such as aqueous acetic acid, aqueous ethanol or those found directly in fatty foods, for example olive oil, are usually used to study the overall migration of these compounds (Kashtock and Breder, 1980; Ashby, 1988; Castle et al., 1989). Commission Regulation no 10/2011 specified SMLs for ethylene glycol and BHET of 30 mg/kg and 60 mg/kg, respectively.

2.2 Traces of metals.

Inorganic species may be present as residues from the catalysts or additives used to produce PET. It is known that Sb_2O_3 is the most important catalyst used in the synthesis of PET (EU, 2008). Concentrations of antimony (Sb) were found in the range of 168 to 216 mg/kg in four brands of PET bottles (Nishioka et al., 2002). Westerhoff et al. (2008) detected 213 mg/kg of Sb in one PET bottle brand after microwave digestion and Keresztes et al. (2009) found between 210 and 290 mg Sb/kg in 10 different brands.

Ti and Ge based catalysts are also known to be used. Westerhoff et al. (2008) have analyzed 23 metals in PET bottles. The highest concentrations were found for Co, Cr, Fe, and Mn, with 27 mg/kg, 0.11 mg/kg, 1.3 mg/kg, and 0.34 mg/kg, respectively. The relatively low levels of these concentrations observed in the polymeric material as compared to Sb, explain why so few studies have been made of the migration of these trace metals into bottled drinking water.

The following subsections present studies of the migration of these inorganic species from PET to bottled water. The results are discussed separately for antimony and the other trace metals taken together. The results of all reviewed studies of Sb migration into PET-bottled water are shown in Table 1.

2.2.1 Antimony.

Ashby (1988) has investigated the effect of various parameters (food simulant, exposure temperature, and exposure time) on the migration of Sb. Even at a high temperature (230°C for 2 h), Sb has low levels of migration (less than 10 µg/L). Shotyk et al. (2006) found unambiguous evidence of Sb leaching from PET containers by studying 63 brands of bottled water coming from Canada and Europe. Comparisons with analyses of the pristine groundwater and the same water available in glass bottles, in which there is no antimony, have confirmed that water is polluted by PET containers. The median Sb concentration in the European bottled waters was 0.343 µg/L, the maximum value being less than 0.8 µg/L. In another publication, Shotyk and Krachler (2007), authors found an Sb concentration of 2 µg/L or more in two brands of PET-bottled water. They also studied the effect of storage time. After a period of 6 months at room temperature, Sb concentrations were found to have increased by 90% on average in 48 brands of bottled drinking water from European countries. In contrast, using 9 commercial brands of bottled water purchased in Arizona, Westerhoff et al. (2008) did not find any statistical differences with samples stored at 22°C after 3 months. On the other hand, they did establish that high temperature storage had a significant effect on the release of Sb. Those results were confirmed by Keresztes et al. (2009) and Cheng et al. (2010). In contrast, both authors concluded that sunlight irradiation has a lower effect on Sb leaching than temperature.

Concerning the influence of bottle color, Westerhoff et al. (2008) observed that the release of Sb into ultrapure water was 4 times greater with clear PET bottles than with blue-colored ones. In their study, equal dimensions of the two PET samples (clear and blue) were incubated in 1L of ultrapure water at 60°C for 10 days. In contrast, Reimann et al. (2010) observed that Sb leaching increases with dark colored bottles as compared to clear bottles. Surprisingly, Sb was also detected by Reimann et al. (2010) in water in dark green glass bottles but in smaller concentrations than in PET. The main reason for its appearance in glass bottled water is that

Sb_2O_3 is usually used in small quantities as a refining agent in glass manufacturing to remove gas bubbles and to obtain more homogeneous glass (Doremus, 1994).

Ten different Hungarian brands of PET-bottled still mineral water and sparkling mineral water were investigated by Keresztes et al. (2009). Authors have demonstrated that Sb leaching increases rapidly during the first storage period and then the Sb diffusion reaches a “steady state”. They have also noticed that the rate of Sb dissolution into water was higher into sparkling water than into still water, due to the lower pH of the carbonated water. The higher release of Sb due to the pH (pH = 4.0) was also observed by Cheng et al. (2010), who also detected the lowest Sb concentrations in ultrapure water contained in washed PET bottles. The authors concluded that the Sb in the bottled water came not only from the PET material but that the water had also been partially contaminated during the bottling process.

Keresztes et al. (2009) have shown, as was expected, that the Sb level in bottled water depends on the contact surface area. Higher concentrations were found in smaller bottles. Sometimes, the migration experiments were carried out by placing plastic test samples in an appropriate container with a known volume of food simulant. Migration levels were not directly obtained by analyzing the Sb concentration in the water of a capped bottle, but by using the ratio between the sample surface area and the volume of eluted solution (Nishioka et al., 2002).

2.2.2 Other metals.

Few results have been reported from the leaching of other trace metals into PET-bottled water. Ashby (1988) investigated the Co migration from PET bottles stored for 10 days at 40°C. The Co concentration in water was below the method's detection limit (< 3 µg/L). Recently, Cheng et al. (2010) assayed the release of 15 inorganic elements (Al, V, Cr, Mn, Co, Ni, Cu, As, Se, Mo, Ag, Cd, Ba, Tl, Pb) in 5 different brands of commercial bottles

subjected to different conditions (low pH, outdoor sunlight irradiation, in-car storage, cooling, heating and microwave treatment). No significant traces of these metals in water were found by the authors. Reimann et al. (2010) found more metals leaching from glass (Ce, Pb, Al and Zr) than from PET bottles.

To summarize this section on metal traces in PET-bottled water, all of the studies agreed that Sb is the most relevant element leaching from PET bottles. The main reason is that antimony trioxide (Sb_2O_3) is widely employed as a catalyst in the synthesis of PET (Welle and Franz, 2011). Only a small fraction of the Sb contained in PET is released into the water (Nishioka et al., 2002). Welle and Franz (2011) have simulated migration as a function of the amounts of Sb in PET bottle wall (224 and 350 mg/L) and with different water volumes (500 to 1500 mL). With identical contact conditions it was shown that higher bottle volumes released lower levels of Sb. According to the authors, the Sb diffusion in the worst case of exposure never reached the SML laid down in the European packaging regulation. Data given in Table 1 never exceeded the SML of 0.04 mg/kg prescribed for this compound in the European legislation (EU, 2011).

A review of the literature shows that the Sb diffusion increases with temperature, storage time and low pH. Also, all authors agree that the migration appears to be less significant as a function of sunlight exposure of PET containers than of the other factors. However, there were contradictory conclusions concerning the effect of bottle color on Sb migration. Whereas Westerhoff et al. (2008) detected an increase in the Sb concentration in clear PET bottles as compared to colored ones, Reimann et al. (2010) concluded the opposite.

2.3 Carbonyl compounds.

Several carbonyl compounds have been reported to be present in bottled drinking water and in PET packaging. Volatile organic compounds are generated in PET by thermal degradation. .

Acetaldehyde is generated during the polymerization reaction and the melt process during manufacturing of PET bottles. The scission of the polymer chain bonds leads to the formation of carboxyl and vinyl ester chain ends. Acetaldehyde is formed by the combination of these two end groups as a reaction sub-product (Lorusso et al. 1985; Romão et al., 2009b).

Formaldehyde is formed by an internal cleavage of the polymeric chain (Kovarskaya et al., 1968).

2.3.1 Carbonyl compounds in PET raw material, preforms and bottles.

When investigating amounts of carbonyl compounds in PET containers, Dong et al. (1980) detected acetaldehyde levels between 0.5 µg/g and 6 µg/g in PET bottle-grade resins. Popoff and Pujolle (1988) reported average acetaldehyde levels in pellets of between 3.12 and 2.6 µg/g and in preforms of 0.75 µg/g by means of an inter-laboratory test. These authors identifies some parameters that could influence the level of acetaldehyde in PET bottles, namely, the humidity of pellets, the injection time and temperature required to produce preforms. They also pointed out the importance of controlling temperature during the injection of preforms, since if the temperature rises by a few degrees then preforms with an acetaldehyde concentration higher than 10 µg/g can be generated. Furthermore, Villain et al. (1994) and Choodum et al. (2007) confirmed that the amounts of acetaldehyde and also formaldehyde in industrial PET were highly dependent on the molecular weight of the polymer and bottle-blowing temperature.

Eberhartinger et al. (1990) found that acetaldehyde levels in PET bottles ranged between 1.31 µg/g and 5.65 µg/g which is slightly higher than the results of Linssen et al. (1995). The latter authors detected acetaldehyde levels ranging from 1.7 µg/g to 3.8 µg/g in mineral water in PET bottles. Also, Mutsuga et al. (2005) found acetaldehyde levels in PET bottles from Japan, Europe and North America in ranges of 8.4 - 25.7 µg/g, 5.0 - 13.1 µg/g and 9.1 - 18.7 µg/g,

respectively. Traces of formaldehyde were also found, ranging between 0.8 - 3.0 $\mu\text{g/g}$, < 0.5 $\mu\text{g/g}$ - 1.6 $\mu\text{g/g}$ and < 0.5 $\mu\text{g/g}$ - 1.2 $\mu\text{g/g}$ in the same Japanese, European and North American containers, respectively. The highest levels of formaldehyde and acetaldehyde in Japanese bottles were attributed to the difference in formulations and in packaging production. In contrast, bottle color does not appear to affect the levels of these two compounds.

To our knowledge, other carbonyl compounds traces have not been found in bottle-grade PET.

2.3.2 Studies of migration of carbonyl compounds into PET-bottled water.

The studies of diffusion of carbonyl compounds from the wall of PET bottles to water aimed to determine significant factors (contact time, temperature storage, light exposure, physico-chemical properties of drinking water, etc.) that can promote their migration from polymer into bottled water.

A review of the scientific literature showed that the migration of acetaldehyde into bottled water has been widely investigated. However, only a few publications have been devoted to studying the presence of other carbonyl compounds (formaldehyde, propanal, butanal, etc.) in bottled water.

The occurrence of the migration of all carbonyl compounds into PET-bottled drinking water will be reviewed as a function of the significant factors affecting migration, as tested by authors. The results of these studies are given in Table 2.

Influence of contact time, temperature, pH and CO₂ of bottled water.

The first migration studies focused on acetaldehyde to try and explain undesirable taste and odor in bottled water. Pepin et al. (1983) examined the relationship between the detection thresholds of this compound in carbonated mineral water and the initial concentrations in the

PET bottle wall after maximum exposure of 3 months at 25, 37 and 45°C. The use of three grades of PET containers, with acetaldehyde concentrations of 3.0 mg/L, 6.8 mg/L and 8.8 mg/L, proved that the migration was related to the amount of acetaldehyde in the bottle wall and that it was directly dependent on temperature and time of storage.

Porretta and Minuti (1995) found trace amounts of acetaldehyde in 34 different brands of drinking water purchased from retail outlets. All of the samples of 16 brands of still water exhibited levels of acetaldehyde above the taste threshold of 15 µg/L after 9 months of storage at 42°C. In contrast, Nijssen et al. (1996) found that acetaldehyde levels in still mineral water in PET bottles were lower than the method detection limit (LOD = 0.5 µg/L) after 12 weeks of storage at 30°C. Their stability experiments were carried out at room temperature with the addition of acetaldehyde in still mineral water, boiled still mineral water, still mineral water adjusted to pH = 3.7 and carbonated mineral water stored in PET and glass bottles. In all cases, the results showed a decrease of acetaldehyde level in still water over time. The authors suggested that oxygen or traces of metal ions in still mineral water could promote the degradation of acetaldehyde. They indicated acetic acid, acetic anhydride, peracetic acid and trimer paraldehyde as possible products resulting from the oxidation or/and the reduction of acetaldehyde. The stability of formaldehyde and acetaldehyde was also investigated by Mutsuga et al. (2006) in sterilized and unsterilized mineral water. The authors observed that these two compounds disappeared in commercial mineral water stored at 40°C over time and explained this as being due to heterotrophic bacteria, which are able to decompose these compounds.

Lorusso et al. (1985) confirmed that a certain level of CO₂ promoted the release of acetaldehyde from PET to water. After six months of storage, levels of acetaldehyde in carbonated water increased to 100 µg/L in samples kept at room temperature and at 40°C, whereas acetaldehyde was not detected in distilled water under the same experimental

conditions and with the same kind of bottles. Nevertheless, the authors claimed that the levels found in water did not constitute a health hazard according to the Tolerance Daily Intake (TDI) of 6 mg/L (calculated for a person weighing 60 kg) established by the EEC Scientific Committee for Human Feeding in 1983. In contrast, the values found to exceed the organoleptic detection limits for acetaldehyde in water ranged between 4 and 65 µg/L according to the authors.

Only Nawrocki et al. (2002) found nonanal, glyoxal and methylglyoxal and particularly, acetone in different series of samples of bottled water available in Poland directly from a local market. As previously reported by Nijssen et al. (1996), they have also shown, particularly with acetaldehyde, that lower pH associated with CO₂ significantly increased the amounts of these compounds in water. Whereas, after long-term storage (8 to 9 months) they found a decrease in acetaldehyde concentration levels. According to Nawrocki et al. (2002) this phenomenon was linked to the gradual loss of dissolved CO₂ as the bottles are not sufficiently tight for the gas. The carbonyls compounds diffuse through the bottle wall similarly to CO₂. The influence of carbon dioxide content in bottled water was also studied by Dabrowska et al. (2003). After several experiments, the authors concluded that the CO₂ itself was not responsible for the higher amounts of acetaldehyde in bottled water. Actually, it was assumed that the pressure exerted by the gas on the PET wall promoted the diffusion. Another experiment carried out with pieces of PET in contact with de-ionised water at pH 4.5 and 6.5 also revealed that low pH did not enhance the migration.

Using another approach, Ewender et al. (2003) studied the short and long-term diffusion of acetaldehyde into carbonated and non-carbonated mineral water in 11 refillable and non-refillable PET bottles. They noticed that the carbonation of water directly influences the diffusion and the stability of acetaldehyde in mineral water as shown by Lorusso et al. (1985), Porretta and Minuti (1995) and Nawrocki et al. (2002).

In complete contrast to the other publications, Ceretti et al. (2010) did not detect any acetaldehyde in 6 commercial brands of still and carbonated mineral water in PET bottles. Samples were stored at 40°C for 10 days according to the standard migration protocol recommended by European Economic Council Directives No.82/711/EEC and No. 93/8/EEC.

Influence of the manufacturing technology and bottling process.

Levels of formaldehyde, acetaldehyde, propanal and butanal in commercial mineral water coming from different countries were determined by Sugaya et al. (2001). However, the fact that these 4 aldehydes could not be detected in some samples (3 samples from France and 2 Japanese products) suggested that the presence of these compounds in mineral water depends on the quality of the PET container and the bottling process. Certainly, the chemical quality of PET bottles depends on the raw material and on the technology used for manufacturing the packaging, Pinto and Reali (2009).

Later on, another research group Dabrowska et al. (2003) thoroughly investigated aldehyde contamination in mineral water in an attempt to explain the origin of these compounds and the parameters affecting diffusion. A production line of carbonated mineral water was monitored. Each step in production of the bottled water from raw water to the finished product was evaluated. The appearance of formaldehyde, acetaldehyde, propanal, nonanal and glyoxal was observed in ozonated water used to disinfect the bottles. This step appeared to be a source of pollution for the PET material and it could be responsible for some carbonyl compounds pollution of mineral water. But the total aldehyde level (3.2 µg/L in the finished product) was very close to the analysis background. In contrast and in comparison with glass bottles, higher levels of formaldehyde and acetaldehyde were found in water originated from PET bottles after 170 days of storage. These phenomena confirmed that the PET container generates these two compounds.

Polypropylene caps were also tested by Dabrowska et al. (2003). Pieces of them were stored in de-ionized water at 20°C and 60°C for several hours. Formaldehyde, acetaldehyde and acetone were detected in the de-ionized water and their levels increased over time and with a rise in temperature. The authors concluded that polypropylene caps were a source of carbonyl compound contamination, and particularly acetone, in bottled water, but with less effect than PET packaging.

Up to now, only these authors have detected acetone in water in PET bottles and they have indicated that acetaldehyde and acetone are equally important carbonyl compounds migrating to bottled water, whereas the source of glyoxal, methylglyoxal and nonanal has not yet been clearly established. Their presence was rather attributed to the origins of the samples and the different kinds of manufacturing processes.

Influence of exposure to sunlight.

Wegelin et al. (2001), in order to test the efficiency of Solar Water Disinfection (SODIS) studied the formation of photoproducts and their migration in water in PET bottles exposed to sunlight. They observed an increase in the concentration of formaldehyde in the bottled water over the exposure time up to an irradiation rate of 313 kWh/m². Surprisingly, samples subjected to the maximum irradiation rate (548 kWh/m²) had the same level of formaldehyde as unexposed ones. In contrast, Nawrocki et al. (2002) observed an increase of formaldehyde, acetaldehyde and acetone in carbonated water stored in PET bottles exposed over time to sunlight and ambient temperature.

Using another approach, Strube et al. (2009) investigated UV-light degradation products of fatty acid amides as a source of plastic off-odors in packed mineral water. They identified 14 carbonyl compounds including hexanal, octanal, nonanal and decanal after exposure to natural sunlight.

After reviewing the literature on the presence of carbonyl compounds, the following conclusions can be drawn:

- The main source of formaldehyde and acetaldehyde in bottled drinking water is PET packaging. Their concentrations in the PET bottle wall depend on the formulations of raw material and on the manufacturing technology used (production of granules, preforms and bottles).
- Most authors agreed that the diffusion of formaldehyde and acetaldehyde was affected by temperature, storage time and carbonation of water associated with the lower pH in bottled drinking water. However, opposite conclusions about the increase or decrease of the amounts of these two compounds following exposure to sunlight have been drawn by Wegelin et al. (2001) and Nawrocki et al. (2002).
- In some diffusion studies, different authors observed a disappearance of acetaldehyde and also, formaldehyde in commercial still mineral water. The degradation of these compounds by oxygen, traces of metal ions or heterotrophic bacteria present in still water were the main reasons given by these authors to explain the phenomena.
- Other carbonyl compounds have been detected in PET-bottled drinking water, namely: propanal, butanal, nonanal, glyoxal, methylglyoxal and acetone. However, the different steps in the bottling and bottle capping processes could be the source of these compounds in drinking water.

Nevertheless, the LMS (EU, 2011) values established for formaldehyde and acetaldehyde of 15 mg/kg and 6 mg/kg, respectively, were never observed in the studies of PET-bottled water reviewed (Table 2).

2.4 Plasticizers.

The addition of plasticizers to plastic resins is widespread, to improve their softness and flexibility, especially in Polyvinyl Chloride (PVC) up to 20-30% (Mori, 1979). Di-2-EthylHexyl Phthalate (DEHP) is the most widespread plasticizer produced and employed (Oehlmann et al., 2008). Di-2-ethylhexyl adipate (DEHA) is also commonly employed in PVC products to replace phthalates (Cao, 2010). It has been demonstrated that phthalate esters and also their metabolites induce abnormal reproductive development in animals and that they are endocrine disruptor compounds (Heudorf et al., 2007; Howdeshell et al., 2008).

According to references cited by several authors (FSA, 2007; Franz and Welle, 2009b; Cao, 2010) plasticizers (like phthalates) are not believed to be used for manufacturing PET bottles. Further, phthalates in food contact materials are subject to strict regulations. However they have been found in PET material and in water in PET bottles. In this section, the amounts of phthalates and DEHA detected in PET-bottled water will be reviewed and discussed. The results of these studies are given in Table 3.

2.4.1 Phthalates.

Phthalates have been detected in the atmosphere (Xie et al., 2006), in aquatic environments (Peijnenburg and Struijs, 2006; Oehlmann et al., 2008), and in drinks and food (Cao, 2010). The major problems in analyzing phthalates lie in various sources of possible contamination. One source is the background pollution that may occur during the sample preparation procedure (Tienpont et al., 2005; Fankhauser-Noti and Grob, 2007; Reid et al., 2007). In their study, Higuchi et al. (2004) have shown that Di-n-Octyl Phthalate (DOP) contamination in mineral water was due to the bottling line and not to the PET bottles. Serôdio and Nogueira (2006) were also very cautious regarding the source of Di-Butyl Phthalate (DBP) in mineral water matrices (0.35 µg/L) suggesting that it might come from the PET bottles. Cap-sealing resins for bottled foods have also been pointed out for their role in DEHP contamination (Hirayama et al., 2001). However, in a recent study no traces of

phthalates (DMP, DBP, BBP, DEHP) were detected in water after incubation at 40°C for 10 days (Ceretti et al., 2010; Guart et al., 2011). Further, the presence of phthalates in glass-bottled water confirmed that they might come from water treatment facilities, namely: pipes, storage tanks and filtering systems (Montuori et al., 2008; Leivadara et al. 2008).

However, several reports have claimed that migration from PET bottles could be the explanation for phthalates in bottled water. Mori (1979) was one of the first authors to investigate contamination by phthalate esters (DBP, DEHP and diethyl phthalate (DEP) in water kept in 100-mL bottles. Kim et al. (1990) used Soxhlet extraction with absolute ethanol for 48 hours to achieve a maximum level of migration from amber-colored PET bottles and identified phthalates such as DEHP, DBP and DEP at levels of 820 µg/g polymer, 220 µg/g polymer, and 120 µg/g polymer, respectively. The source of these compounds was attributed to the coloring substance. Comparing the results of analyses of bottled water before and after storage, Casajuana and Lacorte (2003) concluded that poor storage conditions (10 weeks outdoors at temperatures of up to 30°C) increased the concentrations of DBP, BBP and DEHP in bottled water. After exposure, the mean concentrations of DBP, BBP and DEHP were 0.046 µg/L, 0.010 µg/L and 0.134 µg/L, respectively.

Montuori et al. (2008) are the only authors who investigated the presence of phthalic acid (PhA) in water in PET bottles apart from DMP, DEP, DiBP, DBP and DEHP. Their results showed that PhA was the most abundant phthalate found in bottled water with a maximum level of 3.50 µg/L. They also found that the concentrations of phthalates in samples bottled in PET were 20 times higher than in those from glass bottles directly analysed after purchase. They found no correlation between physicochemical water properties and phthalates migration. Nevertheless, in still mineral water higher phthalates levels were detected than in sparkling water. However, they offered no explanation for this. In contrast, Cao (2008) did not observe significant differences of phthalate levels between glass bottled water and

drinking water in PET containers. Furthermore, they found no significant changes between phthalates migration into carbonated and non-carbonated water.

The effect of other parameters on phthalates migration has been studied by Bošnjir et al. (2007). The concentrations of phthalate appeared to be influenced by the pH level of beverages. Phthalate concentrations were between 5 to 40 times higher in soft drinks (pH = 3) than in mineral water (pH =5). The authors suggested that acidic pH stimulates diffusion of phthalates.

As regards sunlight exposure experiments, Schmid et al. (2008) detected DEHP (100 - 710 ng/L) at a level 7 times higher than for the blank samples (110 ng/L). In this study, the authors concluded that the contribution of plasticizer migration was not significant. Amiridou and Voutsas (2011) have also conducted experiments with PET bottles under outdoor conditions. They detected low traces of DEP (33 ng/L) and DBP (44 ng/L) and higher concentrations of DEHP (350 ng/L) in PET-bottled drinking water.

Several studies have yielded data on the content of phthalates in bottled water immediately after purchase, but without examining the migration parameters (time and storage conditions). The initial levels were frequently lower than 0.4 µg/L (Page and Lacroix, 1995; Peñalver et al., 2000; Kayali et al., 2006; Montuori et al., 2008).

2.4.2 Di-2-ethylhexyl adipate (DEHA).

Kim et al. (1990) identified DEHA in amber-colored PET bottles with a maximum amount of 560 µg/g in PET obtained by Soxhlet extraction. The authors reported that this value represented the maximum migration level into food. However, it was assumed that this level would be never reached under actual storage conditions.

Investigation the occurrence of DEHA in bottled drinking water, Serôdio and Nogueira (2006) found that DEHA concentrations in bottled water (0.15 µg/L) were slightly higher than in tap water (0.09 µg/L). In contrast, DEHA was above the method detection limit of 17 ng/L in all carbonated and non-carbonated samples analysed by Cao (2008).

The influence of sunlight exposure and temperature related to DEHA levels in PET-bottled water was investigated by Schmid et al. (2008) in a SODIS treatment of water. The differences in DEHA concentrations in bottled water were observed in relation to increased temperatures and samples from different countries (Honduras, Nepal and Switzerland) were compared. The highest DEHA level of 0.044 µg/L at 60°C with sunlight exposure was found in PET bottles from Honduras.

Following a review of reported studies in the literature, it should be noted that the phthalate esters and DEHA were found to have a wide range of concentrations in bottled water depending on the study in question. One reason could be the sample extraction methods used. The traditional methods (liquid-liquid extraction) led to high background levels and also a high risk of external contamination, whereas solid phase extraction (SPE) and solid-phase micro-extraction (SPME) generated more accurate data at lower detection limits. The contrasting results in the literature may also be due to numerous other factors, such as the small number of samples studied, the PET bottle grade quality and differences in the storage conditions (contact time, temperature and light). Another possible explanation is the large variation in the use of plasticizers in the packaging industry over time as reported by Balafas et al. (1999). Samples from the same brands of PET directly purchased in the market were analyzed in 1996 and in 1997. Total phthalate concentrations in the polymer decreased from 138 µg/g to 84 µg/g over a period of 12 months. More recently, Guart et al. (2011) did not find any phthalate in PET samples. However the absence of plasticizers in packaging material does not necessarily mean that these compounds will be absent in packaged food (Page and

Lacroix, 1995). Up to now however, the origin of these compounds has not been clearly established.

To conclude, it is important to notice that phthalate esters and DEHA observed in the reviewed studies did not exceed the LMS of (EU, 2011). This regulation set up an LMS of 0.3 mg/kg, 30 mg/kg, 1.5 mg/kg and 18 mg/Kg respectively for DBP, BBP, DEHP and DEHA.

2.5 Antioxidants.

The oxidation and photo-oxidation of polymeric material can be inhibited or reduced by using this kind of stabilizer. Small amounts of these substances can be added to the polymer before it is processed. The most widespread antioxidants are hindered phenol inhibitors. However, PET bottles intended for water are usually processed without antioxidants. The addition of triphenylphosphite, triphenylphosphate or Irganox 1222 has only been used in PET fibers to improve their hydrolytic stability (Zweifel, 2001).

2.5.1 Alkylphenols.

In food packaging manufacture, tris(nonylphenyl) phosphite (TNPP) is used as an antioxidant additive to stabilize several polymers such as rubbers, styrene, vinyl polymers and polyolefines. The oxidation of this additive generates 4-nonylphenol (NP) (McNeal et al., 2000). Another source of NP and also octylphenol (OP) comes from the degradation of polyethoxylated nonylphenols (APEOs). APEOs are surfactants that are widely used as cleaning agents in bottle manufacturing; Casajuana and Lacorte (2003). NP is widely found in the environment and known to be an endocrine disrupter (Thiele et al., 1997; Loos et al., 2007; Baugros et al., 2009).

The diffusion studies of NP have focused on PVC and polyethylene (PE) containers (Kawamura et al., 2000; Howe et al., 2001). However, the presence of NP and OP has also

been investigated in drinking water packaged in PET, although the use of TNPP is not known to be used for the production of PET bottles. Fernandes et al. (2008) determined the NP amounts in a wide variety of food-contact materials. In the case of PET containers, NP was not detected. The authors emphasized that these compounds could be used as antioxidants in the manufacture of laboratory equipment and materials (vessels, tubes, detergents...). Hence, background amounts have to be controlled when analyzing samples.

No differences in NP amounts (19 – 78 ng/L) as a function of temperature and time (50°C for 8h) were observed by Toyo'oka and Oshige (2000) in 9 types of drinking water bottled in PET. The authors doubt whether PET bottles are a source of alkylphenols. Later on, Loyola-Rosales et al. (2004) determined levels of NP and OP in spring water bottled in PET, HDPE and PVC. The authors concluded that the source of NP was the water itself or pollution during the container washing steps when the packaging was being manufactured. Although traces of NP and OP were found in the same spring water bottled in PVC and HDPE, neither of the two compounds was observed in the same water bottled in PET. The same authors carried out migration experiments with distilled water according to US FDA test protocols. NP and OP were not observed in water stored in PET at 40°C for 240h. Only PVC and HDPE showed an NP migration from polymer to water that depended directly on temperature and time.

The potential migration of NP in PET bottles stored outdoors in comparison to glass bottles was investigated by Casajuana and Lacorte (2003). Water analyses were conducted immediately after samples had been purchased and subsequently exposed for 10 weeks above 30°C. Although, NP was not detected in any sample after purchase, amounts of these compounds were revealed in 3 samples of 5 tested after the storage. In contrast to these results, water in glass bottles showed NP mean high concentrations of 78 ng/L and 1730 ng/L before and after exposure respectively, under the same conditions as the PET bottles, . The authors did not explain the reason for this increase of NP in water in glass bottles , but the

initial presence of this substance in drinking water stored in glass containers has been attributed to surfactants used for washing glass containers before the water is bottled. Amiridou and Voutsas (2011) have also stored bottles outdoors and directly exposed to sunlight for 15 and 30 days. Low traces of NP (around 10 ng/L) and OP (around 2 ng/L) were observed. No significant differences in NP and OP amounts before and after exposure were found in the bottled water. In contrast, traces of NP in 21 brands of drinking water bottled in PVC, PE and PET were observed by Li et al. (2010). Concentrations ranged from 108 ng/L to 298 ng/L in PET-bottled water. However, the daily intake value of NP calculated for a consumption of 2 L per day for an adult weighing 60 kg (USEPA, 2006; USEPA, 2009) did not exceed the tolerable daily intake (TDI) of 5 µg / kg body weight proposed by Nielsen et al. (2000).

More recently, Guart et al. (2011) detected NP and OP only in two of ten samples of PET-bottled water tested. The amounts of NP (19 ng/L) and OP (3 ng/L) found agreed with the results of Amiridou and Voutsas (2011). The authors attributed the occurrence of these two compounds to the use of NP and OP in the specific manufacture of polymers depending on the bottle brands.

2.5.2 Butylated hydroxytoluene (BHT).

BHT is a phenolic antioxidant used in plastic packaging, rubbers, cosmetics and also as a food additive. It is widely used as a thermostabilizer for polyethylene, polypropylene, polyesters and polyvinyl chloride (Sheftel, 2000; Tombesi and Freije, 2002). BHT is on the positive list of the European regulation with an SML of 3 mg/kg.

Kim et al. (1990) identified BHT and its processing breakdown product (2,6-bis-(1,1)-methylethyl)-4-ethyl phenol) in PET commercial amber bottles by means of Soxhlet extraction and gas chromatography/mass spectrometry (GC-MS) methods. However analysis of the PET bottles using another GC/MS methodology and Size Exclusion Chromatography –

High Performance Liquid Chromatography (SEC-HPLC) did not reveal any trace of this compound (Monteiro et al., 1996; Monteiro et al., 1998).

Concerning the occurrence of BHT in PET-bottled water, Tombesi and Freije (2002) found quantifiable amounts of this compound in 5 of 15 samples of PET-bottled water with concentrations ranging between 21.5 – 38.0 µg/L. Later on, the same research group Tombesi et al. (2004) detected BHT in three samples of bottled water but concentrations were ten times lower than in the first studies. The authors claimed that the amounts measured do not exceed the levels recommended by the European Union standards for total phenols in drinking water. Nevertheless, the origin of this compound in drinking water was not discussed. In contrast, Higuchi et al. (2004) found a concentration of 2.5 µg/L of this compound in mineral water bottled in glass but BHT was not observed in the same water bottled in PET. The authors concluded that BHT occurrence in mineral water could be due to the use of PE caps.

2.6 UV stabilizers.

Up till now, Tinuvin P (2-(2H-benzotriazol-2-yl)-p-cresol) and Tinuvin 234 (2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol) are the only UV stabilizers found with direct analysis of PET bottles. Both compounds are light stabilizers and they are generally used in the production of polystyrene, polyamides, polymethacrylate, polyesters, polyvinyl chloride and polypropylene (Sheftel, 2000). The specific migration limits (SML) of Tinuvin 324 and Tinuvin P were fixed at 1.5 mg/kg and 30 mg/kg, respectively (EU, 2011). According to (FSA, 2007) these UV absorbers could generate benzotriazole by a photolysis and photo-oxidation mechanism.

Monteiro et al. (1996) developed a high performance size exclusion chromatography method for the quantification of Tinuvin P in PET containers used for vegetable oils. Concentrations ranging from 0.0122 to 0.0124 g per 100 g of PET were observed. Later on, the same

researchers Monteiro et al. (1998) found this compound in PET bottle material using GC – MS.

Only a few publications have been devoted to the study of the diffusion of Tinuvin P and Tinuvin 234 from the polymer to fatty-food simulants. Their migration into bottled drinking water has not been reported, which appears to be due to the insolubility of these compounds in water. Besides, the diffusion coefficient of Tinuvin 324 experimentally calculated in 95% ethanol at 40°C after 10 days is very low (of the order of 10^{-17} cm²/s) (Monteiro et al., 1999; Begley et al., 2004).

2.7 Lubricants.

Lubricants are another kind of additives that are generally used for the production of plastic packaging in order to minimize the adhesion of food, to reduce friction or to promote the elasticity of the material (Schaefer et al., 2003). A later study confirmed that these additives are used in the manufacture of packaging and also for the maintenance of technological equipment (Čížková et al., 2009). Fatty acid amides are also a kind of lubricant used for the manufacture of polyolefin closures. Lubricants such as erucamide and also oleamide are authorized in Europe for the manufacture of plastic materials intended to come in contact with food (EU, 2011). No SMLs have been prescribed for these substances.

To our knowledge, erucamide and oleamide are not used in the manufacture of PET bottles. However, erucamide could be used in the manufacture of bottle closures to facilitate their removal from the container on opening (Shi et al., 2004). This could explain why they are found in mineral water in concentrations ranging from 2.0 ng/L to 182 ng/L as observed by Buiarelli et al. (1993) and Monteiro et al. 1996. It is important to notice that erucamide could generate oxidation products when exposed to sunlight according to Strube et al. (2009).

2.8 Bisphenol A.

Bisphenol A (BPA) is a moiety used in the manufacture of epoxy resins and polycarbonate plastics (PC) for food packaging (McNeal et al., 2000). It is known to be an endocrine disrupting chemical that may cause harmful effects in animals and probably in humans (Thiele et al., 1997; Berryman et al., 2004). The time and period of exposure to BPA are particularly significant parameters to take into account. Most studies of the release of these substances from food contact materials have focused on PC baby bottles (Biles et al., 1997; Brede et al., 2003; Biedermann-Brem et al., 2008). Few publications have been devoted to the investigation of this compound in PET-bottled water.

Toyo'oka and Oshige (2000) were the first authors to identify BPA in 9 different samples of PET-bottled drinking water purchased in a local market. Concentrations were found to range from 3 ng/L to 10 ng/L. The authors found that BPA concentrations in water remained constant before and after heating PET bottles at 50°C for 8h, and could not therefore incriminate the PET material as a source of BPA. In contrast, a slight increase of 7 ng/L in the amount of BPA after 10 weeks exposure up to 30°C was observed by Casajuana and Lacorte (2003).

As for studies of the influence of sunlight in the migration of BPA into PET-bottled water, outdoor experiments were conducted for 15 and 30 days by Amiridou and Voutsas (2011). Low concentrations (up to 4 ng/L) of BPA were observed in PET-bottled water before and after exposure to sunlight. In contrast, Shao et al. (2005) did not find any BPA in 13 different kinds of beverages, including drinking water, packaged in PET analyzed immediately after purchasing. In contrast, Li et al. (2010) detected traces of BPA in 17 brands of bottled water from China under the same conditions (analyzed immediately after purchase). The concentrations of BPA found in bottled drinking water varied greatly. The concentrations ranged from 17.6 to 324 ng/L. However, the material of which the water container was made

(PVC, PE or PET) was not specified. Furthermore it was suggested that the water itself may have been polluted prior to bottling. Furthermore, another source of BPA in PET-bottled water could be due to the containers' caps. Recently, BPA was identified in unbuffered HPLC water in contact with HDPE, LDPE and PS bottle caps by Guart et al. (2011) using the standard UNE-EN 13130 method to determine the specific migration of plastic materials, whereas this compound was not found in water in contact with PET cuts. The samples were incubated for 10 days at 40°C and the migration levels from the three different caps materials to HPLC water were around 0.1 mg/dm².

In any case, the presence of BPA was surprising because this compound is not used in the production of PVC, PE, PET and PS. Sax et al. 2010 reported that one possible explanation for some compounds not expected in bottled water could be the use of recycled PET.

3 Toxicological evaluation of PET-bottled water.

Only the substances on the positive list established in regulation 10/2011 may be used for the manufacturing of plastic materials intended to come in contact with food. Thus, overall migration experiments must be performed to prove the conformity of plastic material with the regulation. Further, as limits have been fixed for several substances on the basis of their toxicological potential (Severin et al., 2011), specific migration must also be checked.

Although, food contact packaging is tightly controlled by European regulations, it has been suggested that food packaging may leach estrogenic substances (Muncke, 2009; Yang et al., 2011); PET has being pointed out in this controversial subject as a possible source (Pinto and Reali, 2009; Sax, 2010; Wagner and Oehlmann, 2010).

3.1 Cytotoxicity assays.

A biological and chemical approach to PET bottles and to their intermediate components (resins and preforms) in contact with water was performed by Sauvant et al. (1995). PET resins and preforms were incubated in distilled water for 24 h and 10 days at room temperature (20-22°C). The PET bottles were filled with mineral water and the maximum storage time was 24 months at room temperature. Several cytotoxic effects using different endpoints were measured in the murin fibroblasts L-929 cell line, namely: the cellular growth, the lactate dehydrogenase activity (LDH) release, the reduction of the tetrazolium salt 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT), the neutral red incorporation or release of the protein content and the RNA synthesis kinetics.

A significant cytotoxicity was observed in the RNA synthesis, MTT reduction and LDH release assays, when the PET resins and preforms were in contact with distilled water for 10 days. In contrast, no cytotoxic effects in mineral water stored in PET bottles for 24 months were observed. In all cases, no mineral elements and acetaldehyde were detected. The authors thus concluded that only the finished product has to be controlled following the manufacture of PET bottles.

3.2 Genotoxicity assays.

The mutagenicity of non-volatile and volatile compounds in PET mineral water was investigated using the Ames test, by De Fusco et al. (1990). Two independent experiments were conducted with unconcentrated and concentrated water. On the one hand, the PET mineral water was concentrated with silica bonded-phase cartridges after exposure of half of the samples to daylight and the other half to darkness for 1, 3 and 6 months. On the other hand, the test was performed with unconcentrated distilled water in PET bottles exposed at 40°C for 10 days and in daylight for 1 month at room temperature. Concerning the concentrated water extracts, only samples stored for 1 month revealed a mutagenic activity with the *Salmonella* strain TA 98 and with metabolic activation (+S9). The mutagenic activity

was twice as high when samples were stored in daylight (mutagenicity ratio of 3.6). These effects were observed only with the concentrated distilled water whatever the storage conditions and the authors suggested that it was due to the use of a concentration factor. In contrast, Monarca et al. (1994) carried out a GC-MS chemical analysis of non-volatile compounds leached into distilled water and contained in green PET bottles. The diffusion experiments to evaluate the total migration were performed according to the conditions specified in the European Council directives N°82/711/EEC and N°93/8/EEC (40°C at 10 days) and in USFDA (1980) (120°C for 2 hours). Several compounds were detected in distilled water stored in PET bottles, namely: acetaldehyde, acetic acid, propanal, terephthalic acid, dimethyl terephthalate, phenol-2,6-bis(1,1-dimethylethyl)-4,4-methyl and 1,2-benzenedicarboxylic acid butyl-2-methyl-propyl ester. A toxicological assay (Ames test) of carbonated mineral water kept in the same kind of PET bottles was performed. The mineral water was concentrated using silica C₁₈ cartridges after daylight storage (1, 3, 6 months at room temperature). The Ames test results for the concentrated extracts showed no mutagenic activity with *Salmonella* strains TA 98 and TA 100 (with and without S9) whatever the time periods.

Using plant models, toxicities in commercial mineral waters after daylight and temperature exposures were observed by Evandri et al. (2000) and Biscardi et al. (2003). Evandri et al. (2000) performed three different migration experiments under controlled storage conditions. Two brands of still mineral water packaged either in PET or in glass were tested using the *Allium cepa* assay. An increase of the *Allium cepa* chromosomal aberrations was observed in PET water samples exposed to direct sunlight for 16 weeks (twofold induction) and exposed in the dark at 40°C for 10 days (threefold induction). These disturbances were attributed to the migration of volatile compounds into PET-bottled water. However, the results may be not representative because very few PET brands were tested.

Biscardi et al. (2003) compared the presence of chemical compounds in PET-bottled water (still and carbonated) collected directly from the spring source with those filled at a commercial bottling plant. Mutagenicity tests were performed every month in lyophilised mineral water stored in PET bottles during 12 months. On the one hand, the *Tradescantia* micronucleus bioassay was carried out with the addition of distilled water into lyophilised samples. On the other hand, mineral water powder was reconstituted with organic solvents to perform the Comet assay with human leukocytes. In parallel, analyses of the migrants were carried out using GC-MS. It is important to note that lyophilisation is an unusual technique for concentrating water and that the authors did not describe the pre-treatment protocol used for their samples. DCWRRC (1985) described a procedure using evaporation under a low vacuum to obtain a dried solids powder, and this technique makes it possible to keep only non-volatile compounds. An eightfold increase in the micronuclei frequency compared to distilled water was observed for concentrated still mineral water (50-fold) contained in PET bottles after 2 months in storage. Significant DNA damages in human cells were observed only in PET-bottled water collected in the bottling plant. It was suggested that the distribution pipelines in the bottling plant were a source of mutagens in mineral water. DEHP was identified in the water extracts (3.2 mg/L) in still and carbonated mineral water after 12 months in storage. As DEHP is not genotoxic (Butterworth et al., 1984; Dybing, 2002), its presence could not explain the toxic effect observed. Ceretti et al. (2010) found that genotoxic effects could be associated with mineral and CO₂ content of the water using the *Tradescantia* micronucleus test and *Allium Cepa* assay. However, authors concluded that these findings should be regarded with caution because of the small number of samples tested. In contrast, the Human Blood Lymphocytes (HULYs) bioassay was used to evaluate the toxicity of PET-bottled drinking water by Ergene et al. (2008). No significant effect was observed on the sister chromatid exchange for natural spring water and purified drinking water stored in PET for 8

weeks after bottling. Despite this, the same commercial water caused a cytostatic effect on the HULYs culture.

It is important to note that some kinds of water have a lower pH compared to the extracellular media used in bioassays. Furthermore media need to be buffered to prevent false positive responses in the assay due to a change in the extracellular pH. The pH and also the conductivity of water must to be checked to ensure that the physico-chemical properties of water itself are not of the cause of the positive response.

3.3 Endocrine disruptor assays.

Endocrine disruptors are compounds that mimic or antagonize the actions of natural estrogens, and are the most common form of endocrine disruptor activity (NRC, 1999; ICCVAM, 2003, 2006). These compounds alter the hormone system involved in many biological metabolisms and can produce many health-related problems, such as early puberty in females, reduced sperm counts, altered functions of reproductive organs, obesity, altered gender-specific behaviors, and increased rates of some breast, ovarian, testicular, and prostate cancers (Kabuto et al., 2004; Newbold et al., 2004; Della Seta et al., 2006; Patisaul et al., 2006; Patisaul et al., 2009).

Some authors have reported estrogenic activity in mineral water in PET bottles, using bioassays such as the E-Screen (MCF-7 cell line) and Yeast assays (*S. cerevisiae*) expressing the human estrogen receptor α (ER α). Estrogenic activity was also evaluated using a reproduction test performed with mudsnails, *Potamopyrgus antipodarum* (Pinto and Reali, 2009; Wagner and Oehlmann, 2009; Sax, 2010; Wagner and Oehlmann, 2010). All, these studies suggested the presence of endocrine disruptors in PET-bottled water.

Contamination of bottled water by endocrine disruptors could occur at the different steps of the bottling process, namely: untreated groundwater from a spring, supply pipes or the filling

and cleaning of containers in the bottling process (Montuori et al., 2008; Wagner and Oehlmann, 2009; Sax, 2010). Furthermore, for some authors plastic bottle stress (UV radiation and heat) could also be a source of endocrine disruptors (Yang et al., 2011).

The mineral composition of water itself could be a source of estrogenic activity as suggested by Criado et al. (2005) using fungi growth as a model after 5 incubation months in PET-bottled water. Spore suspensions of *Alternaria alternata*, *Penicillium citrinum* and *Cladosporium cladosporioides* were inoculated into 12 PET bottles of natural mineral water and 12 PET bottles of mineralized water (potable water with added salts). They concluded that salts in mineral water could be at the origin of the growth.

Several compounds have been pointed out as being the source of the hormonal activity. As shown in Section 2.4.1, several authors have detected phthalates in PET-bottled water (Casajuana and Lacorte, 2003; Bošnjir et al., 2007; Montuori et al., 2008). Criado et al. (2005) reported that the level of DBP increased by 20% in bottled water after 5 months of storage. However, no *P. citrinum* growth was detected after the addition of a range of concentrations of DBP in sterilized water. Further, phthalates are not used as additives in the manufacturing of PET bottles (ILSI, 2000). Furthermore contamination cannot be excluded in the studies of Montuori et al. (2008) and Bošnjir et al. (2007), as they did not prove the absence of phthalates in mineral and soft drinks before bottling. In any case, even if they had been present individually, the estrogenic activity of these compounds is too weak (Jobling et al., 1995), particularly for DEHP to explain these data.

As reported in Section 2.2.1 Sb was found in PET-bottled water. Sax (2010) mentioned that Sb could be also a source of estrogenicity. Indeed, Choe et al. (2003) observed a high estrogenicity of antimony chloride using the estrogen receptor dependant, transcriptional expression assay and the E-Screen test. However, the most common catalysts used in PET synthesis are based on antimony oxide, not on chloride (Biros et al., 2002; Duh, 2002; El-

Toufaily, 2006). Among others (see Section 2.2 and 2.2.1), Takahashi et al.(2008) reported that antimony trioxide (Sb_2O_3) is initially added in PET synthesis, and that after the polycondensation reaction, Sb could be found in PET as Sb glycolate, either free or bound to the PET polymer chain. In general and in terms of toxicity, it is important to note that the effect of inorganic species depends on their oxidation state with the trivalent form being the more toxic form (Filella et al., 2002). Some works focused on the study of Sb speciation in PET bottles and PET-bottled water. Martin et al. (2010) observed an Sb trivalent form in the matrix of PET bottles using synchrotron X-ray. In contrast, no trivalent Sb was detected in PET-bottled water by Zih-Perényi et al. (2008).

Recently, Yang et al. (2011) reported on the necessity to test the estrogenicity of monomers and additives used in the manufacture of plastics in their original unstressed form and after stressing. The authors claimed that all plastics subjected to “stress” could leach xeno-estrogenic substances, even those that have no estrogenic activity at the initial step (formulation). The estrogenic activity of PET water bottles was evaluated by an E-screen assay using MCF-7 cells. The saline extracts of PET showed estrogenic activity (RME response > 15 %) for all stress conditions (microwave, sunlight, autoclave). However, no chemical analyses were performed in parallel to identify the compounds involved in the observed effect.

For other authors, estrogenicity could be due to the use of recycled PET (Safa, 1999). Sax (2010) suggested that DMP concentration in PET bottled-soda detected by Bošnjir et al. (2007) could be due to the use of recycled PET coming from shampoo bottles and intended for bottling of soft drinks.

Furthermore, the extraction efficiency of estrogen-like compounds from bottled water depends on the water preparation techniques (SPE, evaporation) (Wagner and Oehlmann, 2010).

In each case when biological data were provided, there was insufficient analytical data to enable us to draw a conclusion.

Pinto and Reali (2009) reported low estrogenic activity, but with great variability, in 9 Italian brands of PET-bottled water using a Yeast Estrogen Screen (YES) bioassay. The water samples were concentrated using C18 cartridges and the extracts were dissolved in dimethyl sulfoxide (DMSO). The highest estrogenic activity observed in one brand of mineral water was 23.1 ng/L EEQ. However, with the other brands of mineral water, hormonal activity was often found to be in the same range as for tap water from groundwater and surface water (15.1 ng/L and 17.2 ng/L, respectively).

Another research group, Wagner and Oehlmann (2009) tested 18 brands of commercial PET and glass-bottled water using the yeast estrogen screen (YES) assay. The same water, contained either in PET or in glass, was tested. Compared to glass, a weak increase of the estrogenic activity in PET-bottled water was observed in 3 of 4 brands. The maximum value (75.2 ng/L of EEQ) was obtained with water packaged in a non-reusable PET bottle. A reproduction test with *Potamopyrgus antipodarum* mudsnails was also performed by (Wagner and Oehlmann, 2009) to detect endocrine disrupters. Mudsnails were inserted in PET bottles that had previously been filled with culturing water. The parthenogenetic generation of embryos was investigated. Although the differences were not statistically significant, the authors claimed that the production of embryos per female increased slightly in PET bottles suggesting that estrogenic contamination comes from PET packaging. However, no correlation was observed with the similar brands between both assays and nothing proved

whether the effect was really due to PET or to a contamination. Furthermore, the American Chemistry Council (ACC, 2009) reported that PET is not a source of estrogenic compounds. More recently, Wagner and Oehlmann (2010), in a complement to their previous article, investigated the influence of sample preparation techniques to extract estrogenic compounds from bottled water. The effectiveness of solid-phase extraction cartridges and the evaporation treatment of the water extracts were investigated.

The choice of an appropriate cartridge sorbent for solid phase extraction (SPE) has been shown to be a critical step for detecting estrogenic activity in the bottled water extracts, since the traditional C18 silica cartridges entrap more estrogenic compounds. Concerning the water sample treatment, authors observed a significant difference in estrogenic activity between the extracts evaporated with or without addition of dimethyl sulfoxide (DMSO). Extracts with DMSO showed higher relative proliferative effects (RPE) 4-fold more than the extracts evaporated without DMSO. Therefore, the authors pointed out that volatile organic compounds kept in DMSO could be the cause of the higher estrogenic activity. Using the E-screen assay, the optimized preparation (C18 cartridges + evaporation with DMSO), revealed the highest estrogenic activity, which was 3-fold higher in PET-bottled water than in water packaged in glass.

Franz and Welle (2009b) ruled out PET packaging as being responsible for this hormonal activity observed, using theoretical models of migration with potential xenoestrogenic candidates such as nonylphenol and bisphenol A. According to the authors, the endocrine disruptors alone have too low an estrogenic potency to explain this effect. Consequently, a chemical mixture, or “cocktail effect”, and/or unknown compounds (NIAS) could be at the source of the estrogenic activity observed, with low concentrations of endocrine disruptors giving rise to a synergistic effect (Muncke, 2009).

Again, no analytical data were provided in parallel, underlying the need to combine chemical analysis with bioassays to clearly identify these compounds and to understand the potential risk of exposure for humans. Furthermore, it is very important to check the steps involved and to make a rational evaluation of the observed effect by identifying and quantifying the possible entry pathways of these compounds.

4 Discussion and conclusions

Food contact packaging is tightly regulated. European regulation No 1935/2004 underlines that: “*Any material or article intended to come into contact directly or indirectly with food must be sufficiently inert to preclude substances from being transferred to food in quantities large enough to endanger human health or to bring about an unacceptable change in the composition of the food or deterioration in its organoleptic properties*”. The LMS values established in regulation N° 10/2011 are calculated on the basis of toxicological data.

Contaminants released from food-contact materials are still a controversial subject, especially concerning estrogenic activity, and PET has also been incriminated as seen in this review.

Throughout this paper, it should be noted that authors used different storage conditions to evaluate the migration of compounds from PET into bottled drinking water. Different analytical methods with sensitive detection limits were employed to identify or/and quantify these substances in a large variety of PET bottles. Since migration depends directly on these factors, the comparison of data is difficult, sometimes impossible and often controversial. The same problem is true of the toxicological studies performed on bottled drinking water.

Depending on the type of assay (yeast, human cell lines, snails, *Allium Cepa*, etc.) and sample preparation (lyophilized, concentrated, etc.) different conclusions were drawn. Further, plant systems (*Allium Cepa*, *Tradescandia*) are not considered as primary screening tools by current international guidelines for mammalian systems making extrapolation very difficult (Evandri et al., 2000).

Also, it is important to specify that very few studies combined the chemical water analysis and toxicological evaluation at the same time.

Nowadays, it is well-known and all scientific reports agree, that formaldehyde and acetaldehyde are thermal degradation products of PET and that they could be released into the bottled water depending on certain storage parameters and according to the type of drinking water (Nawrocki et al., 2002; Dabrowska et al., 2003; Mutsuga et al., 2006). It is assumed that Sb, a catalyst residue in PET synthesis, could also migrate into the bottled water (Shotyk and Krachler, 2007; Westerhoff et al., 2008; Keresztes et al., 2009).

Concerning the presence of carbonyl compounds in PET-bottled water, in all studies and for all storage conditions (shown in Table 2), levels of formaldehyde and acetaldehyde, did not exceed the specified migration limits (SML) of 15 mg/kg and 6 mg/kg, respectively (EU, 2011). Despite this, acetaldehyde exceeds the water organoleptic threshold (between 20-40 µg/L). Furthermore, the odor of water stored in PET bottles compared to that of soft drinks, can be detected at very low levels, due to the absence of masking flavor compounds (Pepin et al., 1983; Nijssen et al., 1996).

Apart from these well-known compounds, which are normally not a problem, we may conclude that it is necessary to be cautious before claiming that there is a direct link between PET use and the compounds found in bottled drinking water. PET is the polymer which uses the least additives (ILSI, 2000). Phthalates, nonylphenol, antioxidants, UV stabilizers, lubricants and carbonyl compounds in PET-bottled water could come from several sources, namely: bottle caps, transport pipelines, disinfection agents, background pollution of analytical methods and the bottling process itself or even environmental pollution. Their presence in glass-bottled water as well, as demonstrated by some authors, is another reason to believe in the possibility of their being other sources than PET.

Less is known about NIAS presence (byproducts, impurities, etc.) in PET bottles and these substances can also migrate into bottled drinking water (Skjevrak et al., 2005; Grob et al., 2006; Franz and Welle, 2008; Muncke, 2009). However, this phenomenon is true for all food contact materials.

The cyto/genotoxic effects and the endocrine disruption activities observed *in vitro* by some authors have raised doubts and revealed discrepancies in the debate about the quality and the safety of PET-bottled water.

In terms of estrogenic effect, a “cocktail” effect in bottled drinking water with compounds having low endocrine disrupting properties and/or water mineral content could explain these positive results (Criado et al., 2005; Muncke, 2009).

However, more comparable and reliable information on the chemical mixtures and the effect observed in the PET-bottled drinking water is necessary before concluding that there is a potential human health risk. Bioassays do indicate that there is an overall risk, but the use of these bioassays must be standardized as well as the analysis protocols (CEN-OCDE guidelines, ISO). Further, it is necessary to combine toxicological data and chemical analysis, especially when the responses are positive, and to determine the possible entry pathways and concentration of compounds.

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Table 1 – Results of antimony (Sb) migration from PET into bottled water.

Exposure temperature (°C)	Exposure conditions	Simulant	Other parameters	Concentration mean (µg/L)	Concentration range (µg/L)	References
Refrigerated	24h, darkness	Ultrapure water	-	-	0.846 ± 1.652	Cheng et al. (2010)
Refrigerated	37 days	Groundwater	-	-	0.05 ± 0.017	Shotyk et al. (2006)
Refrigerated (2°C)	150 days	Ultrapure water, pH = 6.5	Water bottled in hard PET	0.003	-	Reimann et al. (2010)
Refrigerated (2°C)	150 days	Ultrapure water, pH = 6.5	Water bottled in soft PET	0.025	-	Reimann et al. (2010)
Refrigerated (2°C)	150 days	Ultrapure water, pH = 3.5	Water bottled in hard PET	0.0085	-	Reimann et al. (2010)
Refrigerated (2°C)	150 days	Ultrapure water, pH = 3.5	Water bottled in soft PET	0.027	-	Reimann et al. (2010)
r.t.	24 h, darkness	Ultrapure water at 100°C	-	-	3.243 – 1.652	Cheng et al. (2010)
r.t.	24 h	Microwave heated ultrapure water	-	-	0.391 – 10.51	Cheng et al. (2010)
r.t.	6 months	Groundwater	-	0.566	-	Shotyk et al. (2006)
r.t.	7 days, darkness	Ultrapure water at pH = 4	-	-	< 0.02 – 3.794	Cheng et al. (2010)
22°C	3 months	Commercial water	-	0.226 ± 0.160	-	Westerhoff et al. (2008)
22°C	< 1 year	Still mineral water	-	0.26 ± 0.160	-	Keresztes et al. (2009)
22°C	< 1 year	Sparkling mineral water	-	0.40 ± 0.22	-	Keresztes et al. (2009)
40°C	10 days	Aqueous simulant	-	-	< 0.03	Nishioka et al. (2002)
80°C	7 days	Commercial water	-	-	14.4	Westerhoff et al. (2008)
-	7 days, sunlight	Ultrapure water	-	-	< 0.02 – 4.611	Cheng et al. (2010)
-	7 days, in-car storage	Ultrapure water	-	-	< 0.02 – 3.08	Cheng et al. (2010)

r.t.: room temperature

Table 2 – Results of carbonyl compounds migration from PET into bottled water. (continued)

Compound Name	Simulant	Exposure temperature	Exposure conditions	Other parameters	Concentration range (µg/L)	Concentration mean (µg/L)	References
Formaldehyde	Mineral water	–	–	–	< 0.5 - 59	–	Sugaya <i>et al.</i> (2001)
	Still water	–	–	Total organic carbon	2.2 – 64.6	–	Nawrocki <i>et al.</i> (2002)
	Still water	–	–	< 2.0 – 2.9 µg/g in PET	< 5.0 – 27.9	–	Mutsuga <i>et al.</i> (2006)
	Still water	r.t.	6 days	–	–	7.1 ± 0.7	Dabrowska <i>et al.</i> (2003)
	Still mineral water	–	63 days, sunlight	–	–	44	Wegelin <i>et al.</i> (2001)
	Still mineral water	–	126 days, sunlight	–	–	1	Wegelin <i>et al.</i> (2001)
	Carbonated water	r.t.	170 days	–	–	60.0 ± 6.0	Dabrowska <i>et al.</i> (2003)
	Carbonated water at pH = 4.5	r.t.	6 days	–	–	10.5 ± 1.1	Dabrowska <i>et al.</i> (2003)
	Carbonated water	–	–	TOC	24.6 – 96.1	–	Nawrocki <i>et al.</i> (2002)
	Carbonated water	–	–	< 0.5 – 0.9 µg/g in PET	< 5.0 – 13.7	–	Mutsuga <i>et al.</i> (2006)
	Carbonated water	–	–	–	–	1.4 ± 0.1	Mutsuga <i>et al.</i> (2006)
	Acetaldehyde	Mineral water	–	–	–	< 0.5 – 59	–
Mineral water		–	–	–	< 0.5 – 260	–	Sugaya <i>et al.</i> (2001)
Mineral water		–	–	–	< 0.5 – 0.9	–	Sugaya <i>et al.</i> (2001)
Mineral water		–	–	–	< 0.5 – 0.3	–	Sugaya <i>et al.</i> (2001)
Still water		–	–	TOC	0.9 – 133.8	–	Nawrocki <i>et al.</i> (2002)
Still water		–	–	< 2.0 – 2.9 µg/g in PET	< 5.0 – 107.8	–	Mutsuga <i>et al.</i> (2006)
Still water		r.t.	6 days	–	–	4.8 ± 0.5	Dabrowska <i>et al.</i> (2003)
Still mineral water		–	63 days, sunlight	–	–	3	Wegelin <i>et al.</i> (2001)
Still mineral water		–	126 days, sunlight	–	–	2	Wegelin <i>et al.</i> (2001)
Still mineral water		40°C	10 days	–	< 2	–	Ceretti <i>et al.</i> (2010)
Carbonated water		–	–	TOC	4.7 – 317.8	–	Nawrocki <i>et al.</i> (2002)
Carbonated water		–	–	0.5 – 0.9 µg/g in PET	< 5.0 – 46.9	–	Mutsuga <i>et al.</i> (2006)
Carbonated water at pH = 4.5		r.t.	6 days	–	–	24.6 ± 2.5	Dabrowska <i>et al.</i> (2003)
Carbonated water		r.t.	170 days	–	–	78.1 ± 7.8	Dabrowska <i>et al.</i> (2003)
Carbonated water		r.t.	5 weeks	CO ₂ content: 3.88 g/L	–	28.0 ± 2.8	Dabrowska <i>et al.</i> (2003)
Carbonated water		r.t.	5 weeks	CO ₂ content: 4.53 g/L	–	52.0 ± 5.2	Dabrowska <i>et al.</i> (2003)
Carbonated water		r.t.	5 weeks	CO ₂ content: 6.40 g/L	–	79.0 ± 7.9	Dabrowska <i>et al.</i> (2003)
Carbonated water		40°C	10 days	–	< 2	–	Ceretti <i>et al.</i> (2010)

r.t : room temperature ; TOC :Total Organic Carbon; n.d.: not detected.

Table 2 – Results of carbonyl compounds migration from PET into bottled water. (continued)

Compound Name	Simulant	Exposure temperature	Exposure conditions	Other parameters	Concentration range (µg/L)	Concentration mean (µg/L)	References
Propanal	Mineral water	–	–	–	< 0.5 – 0.9	–	Sugaya <i>et al.</i> (2001)
	Carbonated water	–	–	–	-	< 0.05	Dabrowska <i>et al.</i> (2003)
Butanal	Mineral Water	–	–	–	< 0.5 – 0.3	–	Sugaya <i>et al.</i> (2001)
Nonanal	Still water	–	–	TOC	0.9 – 11.3	–	Nawrocki <i>et al.</i> (2002)
	Carbonated water	–	–	TOC	0.95 – 7.9	–	Nawrocki <i>et al.</i> (2002)
	Carbonated water	–	–	–	–	< 0.05	Dabrowska <i>et al.</i> (2003)
Glyoxal	Still water	–	–	TOC	–	5.9	Nawrocki <i>et al.</i> (2002)
	Carbonated water	–	–	TOC	–	0.9	Nawrocki <i>et al.</i> (2002)
	Carbonated water	–	–	–	–	< 0.05	Dabrowska <i>et al.</i> (2003)
Methylglyoxal	Still water	–	–	TOC	0.9 – 15.8	–	Sugaya <i>et al.</i> (2001)
	Carbonated water	–	–	TOC	0.8 – 4.6	–	Sugaya <i>et al.</i> (2001)
Acetone	Still water	–	–	TOC	5.1 – 107.6	–	Nawrocki <i>et al.</i> (2002)
	Carbonated water	–	–	TOC	16.8 – 125.6	–	Nawrocki <i>et al.</i> (2002)

r.t : room temperature ; TOC :Total Organic Carbon; n.d.: not detected.

Table 3 – Results of phthalate esters migration from PET into bottled water.

Compound name	Simulant	Exposure temperature	Exposure conditions	Concentration range (µg/L)	Concentration mean (µg/L)	References
DMP	Mineral water	22°C	30 days	< 0.04	-	Bosnir et al. (2007)
	Water	Up to 30°C	10 weeks	< 0.002 – 0.003	0.002	Casajuana and Lacorte (2003)
DEP	Mineral water	22°C	30 days	< 0.04 – 1	0.11	Bosnir et al. (2007)
	Water	Up to 30°C	10 weeks	0.082 – 0.355	0.214	Casajuana et Lacorte (2003)
DBP	Still water	Refrigerated	-	0.08 – 0.32	0.357 ± 0.606	Cao (2008)
	Mineral water	22°C	30 days	< 0.04 – 50	11	Bosnir et al. (2007)
DiBP	Water	Up to 30°C	10 weeks	0.020 – 0.070	0.046	Casajuana and Lacorte (2003)
	Mineral water	22°C	30 days	< 0.005	-	Bosnir et al. (2007)
DEHP	Water	Up to 30°C	10 weeks	< 0.004 – 0.010	< 0.004	Casajuana and Lacorte (2003)
	Dionised water	r.t.	17 hours, darkness	0.14 – 0.24	0.19 ± 0.05	Schmid et al. (2008)
DEHP	Dionised water	r.t.	17 hour, sunlight	0.10 – 0.38	0.26 ± 0.10	Schmid et al. (2008)
	Dionised water	60°C	17 hours, sunlight	0.15 – 0.71	0.36 ± 0.21	Schmid et al. (2008)
DEHP	Mineral water	r.t.	12 months, darkness	-	3220 ± 200	Biscardi et al. (2003)
	Mineral water	r.t.	3 months	< 0.02 – 6.8	-	Leivadara et al. (2008)
DEHP	Mineral water	22°C	30 days	< 0.04 – 50	8.8	Bosnir et al. (2007)
	Water	Up to 30°C	10 weeks	< 0.002 – 0.188	134	Casajuana and Lacorte (2003)
DEHP	Mineral water	Up to 30°C	3 months, sunlight	< 0.02	-	Leivadara et al. (2008)
	Mineral water	22°C	30 days	< 0.04	-	Bosnir et al. (2007)

DMP: Dimethyl phthalate; DEP: Diethyl phthalate; DBP: Dibutyl phthalate; DiBP: Diisobutyl phthalate; BBP: Benzylbutyl phthalate; DEHP: Di-2-ethylbutyl phthalate; DOP: Dioctyl phthalate; r.t.: room temperature.