Original Paper

Persistence and Bioaccumulation of Persistent Organic Pollutants (POPs) in the Soil and Aquatic Ecosystems: Syrian Frontiers in Ecology and Environment

Loai Aljerf* & Nuha AlMasri

1 Department of Basic Sciences, Faculty of Dental Medicine, Damascus University, Damascus, Syria
2 Department of Chemistry, Faculty of Medicine, Syrian Private University, Damascus, Syria
* Loai Aljerf, Department of Basic Sciences, Faculty of Dental Medicine, Damascus University, Damascus, Syria

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Abstract

In Syria, there are no effective chemicals management programmes including any estimation and assessment programmes to screen organic chemicals for bioaccumulation potential from regulatory and resource implications are conducted yet. An important issue of excessive organic hazardous substances exposure of inhabitants living in Barada basin (Southwest) was not investigated. Among these danger substances, Persistent Organic Pollutants (POPs) have specific properties make them possible linger in soil and water for so many years. Considering the Toxic Substances Control Act (TSCA) and enabling activities for the Stockholm convention on POPs related to the national implementation plan for Syria, the current paper presents the results of the analysis of the persistence of chemicals in surface water and ground water samples gathered from different locations in this basin. The study was conducted in 2007-2008, the biodegradability under laboratory and filed conditions were assessed, half-lives of priority pollutants were predicted, and data were monitored and compared. The level of POPs in a larger percentage of the samples exceeded guidelines which results a call for additional protective measures for a sustainable water management for producing clean water involving reduction strategies to mitigate the POPs concentrations in the indoor environment of Barada, and safely destroy them.

Keywords
air pollution, aquatic environment, bioaccumulation, chronic toxic effects, ecosystem, hazardous chemical substances, microorganisms, polynuclear aromatic hydrocarbons
1. Introduction

1.1 Legislations and Regulations to Control Hazardous Materials

The widespread presence of hazardous chemical substances has recently led to the preparation and adoption of legislative measures in order to protect man and the environment against their adverse effects (Collins et al., 2016). Examples are the Chemical Substances Control Law of 2017 in Japan (Noguchi, 2017), the Toxic Substances Control Act (TSCA) of 2013 in the U.S.A. (Bergeson, 2013), the E.C. Directive on the contamination caused by certain dangerous substances which are discharged into the aquatic environment of the community (Cardoso et al., 2014; Vorkamp et al., 2014) of 2014 and the Convention against Chemical Pollution of the Barada basin in Syria of 2000 (Melhem & Higano, 2002; Aliquot & Piraud-Fournet, 2008).

The essential factors in the relationship on which those regulations are based on are (Figure 1):

(1) The quantity of the chemical available for organisms, and

(2) The nature and severity of biological effects.

![Figure 1. Relationship between a Chemical Compound Released into the Environment and the Biological Effect](image)

As roughly 20,000 chemicals are produced in the world at quantities of 10,000 tons/year or more (Burton, 2004), it is an impossible task to regulate all these chemicals at short notice. In order to set priorities, two approaches are often used. One is based on selecting those chemicals which are produced in the largest quantities. The other selects those compounds which are already known or which can easily be shown to exert acute or chronic toxic effects.

Generally, production data and estimates of the amounts likely to be released into the environment as well as acute toxicity data can be obtained rather easily. Data on bioaccumulation are even scarcer but methodologies to estimate the potential bioaccumulation have been developed quite successfully (Costanza et al., 2012).
1.2 Concepts

1.2.1 Processing Determining the Persistence of Chemical Compounds in the Aquatic Environment

A. Definition

The persistence of a chemical in the aquatic environment is sometimes considered as a characteristic of the chemical compound which can be easily assessed by a biodegradability test. Others have recently developed systems for hazard evaluation of chemicals based on estimating the distribution of a chemical in the air, water and soil (Däumling, 2012). Such information however only gives a partial answer to the question how much of a quantity of the compound released actually remains available in the water phase to various organisms and in what concentration (Figure 1). As the answer to this question is the ultimate purpose of assessing the persistence of a compound in the environment, all processes affecting its concentration at a certain time and a certain location have to be taken into account. Therefore, the following definition of persistence of an aquatic pollutant is proposed:

“The persistence of an aquatic pollutant is the capability of the chemical in the aquatic ecosystem considered to resist a reduction of the original concentration in the water phase after a certain period of time, while undergoing a variety of physical, chemical and biological processes”. A first consequence of this definition of persistence is that the persistence does not only depend on the type of chemical but also on the type of ecosystem concerned. The persistence of a chemical in ground water will be quite different from that in surface water, as will be discussed in more detail below.

1.2.1.1 Ground Water

A. General aspects

Major causes of chemical pollution of ground water in an environmental unit can be (Figure 2):

- Inflowing ground water,
- Local man-made releases by means of waste dumps, spillages,…etc.,
- Natural production in the soil from plant residues,
- Dissolution of adsorbed or precipitated material, and
- Wet or dry deposition.

The last two causes, which represent a recycling of existing pollution, may complicate the study of persistence of a pollutant under field conditions. Particularly, data on the contribution of air pollution to ground water contamination are scarce.
Examples of compounds probably introduced into ground water by natural production processes are certain lower esters and aldehydes like decanal, which were detected in otherwise unpolluted ground waters in Syria (Unpublished data).

Pollutants dissolved in ground water as well as surface water can be reduced in concentration by chemical and biological degradation processes. A major process determining the persistence of pollutants in ground water is the interaction with the solid phase. Volatilisation may also play a role in this respect.

A.1 Biological degradation

Although microorganisms are potentially capable of decomposing most foreign organic compounds, there are large differences in decomposition rates, e.g., between hydrocarbons on the one hand and polychlorinated substances like PCBs and DDT on the other. Most studies relating to biological degradation of organic chemicals in the soil have been carried out in relation to the problem of persistence of pesticides. An extensive survey of the different types of microbial reactions with chemicals occurring in the soil is given by Hess et al. (1996). Hess suggests that the main factor controlling the decomposition rate is the rate of transport of the compound through the cell membranes of the microorganisms. Within the cells, an almost infinite variety of reactions is available which take place at substantially greater rates than the membrane penetration rate.

In general, biodegradation of pollutants in the soil will be further controlled by their water solubility. A logical consequence is that biodegradability will be dependent on climate factors such as temperature and rainfall and on soil factors such as water content, pH, percentage of organic matter and clay, and on
sand and silt distributions. Furthermore, the presence of oxygen or oxygen containing compounds is an important factor in relation to oxidative mineralisation processes. Various tests have been developed to measure the biodegradability of compounds under laboratory conditions (Hongwei et al., 2006; Urgun-Demirtas et al., 2007). Xie et al. (2017) showed that the degree of biodegradation of a compound seems to be test-specific. Synergistic and antagonistic effects, occurring under field conditions, are difficult to detect by laboratory testing.

A.2 Chemical degradation

Literature on the chemical degradation of organic chemicals in ground water is practically non-existent (Díaz-Cruz & Barceló, 2008). In principle, hydrolysis, oxidation and reduction reactions can take place at the surfaces of, e.g., clay minerals, which might exert a catalytic activity. It is generally assumed that biodegradation processes dominate the decomposition of chemicals in ground water.

A.3 Adsorption and precipitation

A major process of reduction of organic chemicals in ground water is adsorption on the large surface of the solid phase (Aljerf, 2018a, 2018b). A wide range of phenomena are included such as ion exchange, hydrophobic bonding, hydrogen bonding and chemisorption. Ion exchange may involve both cations and anions but the cation exchange capacity of a soil usually exceeds by far the anion exchange capacity in the normally occurring pH-range of 4-8. Precipitation of organic acids like oxalates and citrates may be a reversible interaction. Adsorption is largely dependent on the chemical structure of the compounds considered as well as their molecular size, presence of polar or non-polar groups, etc., (Aljerf & Choukaife, 2015). The adsorption process will be further influenced by soil factors such as organic carbon content, water content, pH, cation exchange capacity as well as by the temperature and the salt content of the ground water.

Both adsorption/desorption and precipitation/dissolution may be considered reversible interactions. Precipitation and dissolution often exhibit hysteresis. Solutions generally need a certain degree of undersaturation or supersaturation before salts dissolve or precipitate. Sorption can be studied in the laboratory but many factors are difficult to incorporate in the tests, such as irreversible surface interactions due to occlusion of adsorbed organic chemicals on growing mineral surfaces or fixation between clay minerals like illites. Also, coprecipitation of organic compounds or organo-metal complexes with precipitating substances may occur.

A.4 Volatilisation

Volatilisation of organics from ground water is only relevant in case the contaminated ground water is present near the soil surface for a longer period of time. Substantial losses of pesticides after soil application due to diffusion and codistillation with water have been reported (McAlary & Barker, 1987; Doe, 2013). Generally, the contribution of volatilisation to removal of pollutants from ground water will be relatively small.
1.2.1.2 Surface Water

*General aspects*

Similar causes of pollution and types of reduction processes as described for ground water play a role in the case of surface water. Besides, sedimentation of substances adsorbed on suspended matter has to be considered as well as volatilisation and photochemical degradation (Popenda & Wlodarczyk-Makula, 2018). Chemical degradation reactions (Mozziconacci & Schoneich, 2016) may play a more pronounced role compared to biological degradation processes. Persistence of a pollutant in surface water is the result of an even more complex system of processes than persistence of a chemical in ground water.

**B.1 Volatilisation**

Contrary to the ground water situation, evaporation of volatile organic compounds is a major process of removal in surface water, although part of the evaporated chemicals may sooner or later be introduced into the surface water again by deposition. Examples are the lower hydrocarbons and chlorinated methanes, ethanes and ethylenes (Henson, 1988). The volatilisation process is mainly influenced by the few millimetres above or below the water-air interphase. Evaporation rates depend on properties of the pollutant such as water solubility, vapour pressure, diffusivity, and Henry’s Law constant. Furthermore, the fluid mechanics in the water body and the lower atmosphere are important. According to Wu et al. (2014), the liquid phase resistance to evaporation dominates the mass transfer rate for most hydrophobic pollutants.

In rivers, the vertical transport of pollutants in the water phase is dominated by eddies caused by the interaction of the current with the river bottom and thus by the river depth. In lakes, the turbulence originates from the atmosphere and the wind-speed probably is the dominant parameter. Although, a number of essential characteristics for predicting volatilisation of chemicals are available, difficulties still have to be overcome in the area of rapidly changing conditions in the lower atmosphere resulting in changes in volatilisation rate at a certain location by a factor 10 during a period of several hours. Furthermore, detergents and other surface active materials modify the interracial processes and generally increase the resistance to volatilisation.

**B.2 Photochemical degradation**

Photochemical degradation of chemicals can be the result of direct absorption of sunlight of a certain wavelength by the molecules of the chemical, resulting in molecules in an electronically excited state which react. Also, sensitised photolysis of chemicals occurs by means of photosensitisers such as acetone, benzophenone, and riboflavin. Two types of sensitised photooxidations are found. One type involves H-atom transfer from the chemical to the electronically excited sensitisier or electron transfer, followed by reaction of the resulting free radicals with oxygen or other molecules. The second type of sensitised reactions involves reaction of a sensitisier in a triplet energy state with oxygen to form singlet molecular oxygen which leads to oxygenation reactions of chemicals (Wu et al., 2011).

Jensen and Foote (1988) estimate that in practice, singlet oxygen induced oxidation takes place at
significant rates for organic sulphides, furans, and amino acids. Computed and observed half-life times due to photodegradation for some pesticides like parathion (C₁₀H₁₄NO₅PS, a highly toxic cholinesterase inhibitor that is used as an acaricide and as an insecticide. Exposure may occur from the use of parathion as an insecticide on agricultural crops) and several Polynuclear Aromatic Hydrocarbons (PAHs) varied from 1-100 hours (Matsuzawa, 2000). According to Li et al. (2011), sensitised photolysis proceeds most rapidly in water bodies that are most opaque to sunlight, whereas the opposite is true of direct photolysis.

Although, organic matter will increase the role of sensitised photodegradation of chemicals, it must be realised that such materials also compete with the chemicals considered in the oxidation reactions. As the rate of photochemical degradation directly depends on the dose of light received by the pollutants or sensitisers, factors like latitude, season and time of the day as well as the tendency of the chemical to sorb on suspended matter and bottom sediments are of great influence. In general, direct photolysis rates measured in laboratory experiments can be considerably lower (e.g., a factor 10 or more 24) than rates of photochemical degradation in surface water.

1.2.2 Advantages and Problems of Field Studies vs. Laboratory Evaluation of the Persistence of Chemicals in the Aquatic Environment

As pointed out in the preceding paragraphs, laboratory testing of the behaviour of chemicals in relation to a single degradation process may already lead to results which differ greatly from the situation under field conditions. This problem is made even more difficult by the occurrence in practice of complex combinations of these processes. It seems incorrect to assume that all processes will simply add to a more rapid disappearance of the chemical and its degradation products from the environment. Data of Loretta et al. (2017) illustrate that biodegradation of a chemical may reduce the effect of volatilisation from the soil. Another example is the assumption that volatile lower halogenated organic compounds rapidly evaporate from river water while these compounds persist for many years after infiltration of the water via the river banks into the ground. So, laboratory data may lead to a prediction of the persistence of a chemical in the aquatic environment which can be too low or too high. Therefore, it is felt, as stated by Ech-chafay et al. (2018) that “carefully planned field studies remain the best way for evaluating the behaviour of chemicals in the environment. On the other hand, laboratory studies are needed to be able to understand the ecokinetics underlying the observed phenomena in the field”.

Laboratory data are used to compare chemicals and to estimate which degradation processes are most important. The latter information is essential to indicate which measures are most appropriate to limit distribution of the chemical in the environment. For instance, Lu et al. (2002) found that the disappearance of picloram (C₆H₃Cl₃N₂O₂, a systemic herbicide used for general woody plant control. It controls a wide range of broad-leaved weeds, but most grasses are resistant) in the soil in Brazil was only related to climatic factors and that soil factors could be ignored. Reduction of vinyl chloride (H₂C=CHCl) or chloroform (CHCl₃) in river water is dominated by volatilisation (Ando & Sayato, 1984). Hayet et al. (2016) has pointed at the need to move through a series of stages from a simple
routine biodegradability test to local field trials, designed for the chemical compound under
consideration, in case the margin of safety appears small or the penalty for a wrong decision is large.
Several authors (Madsen, 2003; Nabeoka et al., 2015; Hayet et al., 2016; Kasthuri & Poornima, 2016)
have mentioned disadvantages of field studies such as difficulty and vast amount of analytical work
involved, inadequately defined and constantly varying conditions, etc. These considerations, however,
can only lead to the conclusion that neither field studies nor laboratory studies alone can give a
sufficient basis for legislative measures. Yet, it is amazing, that relatively few data are reported from
field investigations as compared with the growing amount of data obtained from laboratory testing.
Against this background it was considered useful to study existing field data on chemicals in the
aquatic environment in Syria in more detail, although these data were not collected for the specific
purpose of evaluating their persistence.

1.3 Challenge
The problems in selecting the priority compounds are the assessment of their potential long term effects
and their persistence in the environment.

1.4 Aim
In this paper, attention will be given to the challenge aspect which determines whether or not a
potentially toxic chemical released in large quantities will lead to high concentrations in the
environment and to a possible unacceptable exposure of organisms.

2. Method

2.1 Strategy
Persistence in the context of this research will be considered from the point of view of the aquatic
environment only. After describing the processes determining the persistence of chemicals in surface
water and ground water, the problems in estimating the persistence from laboratory tests as well as field
investigations will be considered. Subsequently, field data for organic compounds detected in surface
water and ground water in Syria will be discussed and compared with some relevant data from the
literature relating to laboratory testing. Finally, recommendations will be given to optimise persistency
assessment in the framework of legislating the ecotoxicological risks of chemical compounds.

2.2 Materials and Methods
The values on lower chlorinated hydrocarbons and pesticides were measured in collaboration with the
Arab Centre for the Studies of Arid Zones and Dry lands (ACSAD), at Douma (the centre of Rif
Dimashq governorate and is about 10 km northeast of the centre of Damascus). All
surface waters
considered have a depth of approximately 4-5 metres. On June 2007-August 2008, a careful sampling
of Barada water was carried out for quantification of a wide range of chemicals in the water by means
of GC-MS (Shimadzu QP-5000) of concentrates prepared by closed-loop gas stripping and XAD
adsorption techniques (Espadaler et al., 1997; Xua et al., 2013) (see Table 1). Certified reference
standards from AccuStandard, Inc. (New Haven, CT, USA) was used for the instrument calibration and
quantification of the POPs. Stock solutions were prepared in toluene or in toluene/acetonitrile mixture, and were stored at -18°C in amber coloured glassware. POPs compounds as pesticide grade n-hexane dichloromethane, toluene, ethyl acetate, acetone, cyclohexane, as well as silica gel were purchased from Sigma-Aldrich Chemie GmbH (Buchs, Switzerland). Sulphuric acid and sodium sulphate were obtained from Acros (New Jersey, NJ, USA). Spiking solutions were prepared by serial dilution of stock solutions in toluene and method performance was evaluated by run-to-run \((n=5)\) analyses of spiked matrix at three concentration levels for each compound (e.g., 0.15, 0.30, and 0.75 ng/g w.w.). Accuracy (recovery), repeatability (intra-day precision), instrumental and method limits of quantification (i-LOQs and m-LOQs) were examined during the validation experiments and tabulated. The APCI drying temperature was set to 240°C with nitrogen as nebuliser and drying gas at 3.5 bar pressure and 4L/min flow rate. APCI was operated in positive ion mode with 2000 nA corona current and 3000 V capillary voltage. MS system was operated in full scan mode over the \(m/z\) range of 100-1000 Da in order to provide a more efficient and flexible analytical method with the possibility of post-run processing of raw data.

In order to prevent degradation of potentially photolabile POPs exist in water as the chlorinated and brominated compounds, the sample extraction, clean-up, and handling procedures were performed under UV-protected conditions (e.g., using amber-coloured glassware, wrapping the glassware in aluminium foil). Considering the ubiquity of some of the POPs in the laboratory environment, all glassware was washed with organic solvents before the sample preparation procedures. The quality control criteria for positive identification of the analysed POPs including the retention time of the native compounds within a window of \(+3\) to 0s was compared to the corresponding \(^{13}\text{C}_{12}\)-labeled surrogates. The acceptable deviation of the isotopic ratio for the monitored ions (target/confirmation) was set at \(\pm 15\%\) of the theoretical value. Five-point calibration curves were used for the quantification of analyte concentrations in each sample run. Procedural blanks were included in the Quality Control (QC) protocol and were analysed in each sample sequence during the validation procedures and analysis of certified reference materials. The concentrations of contaminants determined in the analysed samples were corrected by taking into account the analyte concentrations found in procedural blanks.

However, in order to overcome the splitting and defocusing of chromatographic peaks for rapidly eluted compounds representatives and to increase the system performance, a capillary guard column (2 m \(\times\) 0.25 mm) was inserted between the GC injector and the analytical column using deactivated borosilicate glass press-fit connector, allowing to consolidate the uneven injection profiles for compounds with low degree of halogenation. Considering that the maximum possible temperature of the GC-MS transfer line in the current system was 300°C and in order to overcome the possible peak broadening for some of brominated compounds that eluted during the final 320°C plateau of the GC program, a 0.25 mm ID capillary guard column was inserted into the GC-MS transfer line instead of the column. The final GC method ensured elution of all analytes within 25 min.
Table 1. The Optimised Instrumental GC-MS Conditions for Determination of the Selected POPs

| GC conditions                  |
|-------------------------------|
| GC column                     | Rtx-1614 (30 m × 0.25 mm × 0.10 μm) |
| Injection mode                | Splitless                      |
| Injection volume              | 1 μL                           |
| Injector temperature          | 280°C                          |
| Carrier gas and flow          | Helium at 1 mL/min             |
| Oven temperature program      | 80°C for 2 min; ramp to 240°C at the rate of 10°C/min; ramp to 320°C at the rate of 5°C/min; hold for 15 min |

| APCI source conditions        |
|-------------------------------|
| Polarity                      | Positive                      |
| Corona needle current         | 2000 nA                       |
| Capillary voltage             | 3000 V                        |
| Drying gas temperature        | 240°C                         |
| Nebuliser gas pressure        | 3.5 bar                       |
| Spray shield voltage          | -500 V                        |
| Drying gas flow rate          | 4.0 L/min                     |
| APCI head temperature         | 300°C                         |
| APCI transfer line            | 300°C                         |

3. Results and Discussion

3.1 Method Performance

Considering the POP properties, such as bioaccumulation and high lipid solubility, hot extraction was successfully applied for effective isolation of analytes from the matrix. Elimination of the bulk of high molecular mass compounds was achieved by the means of GPC, with further destructive clean-up on acid-modified silica gel and additional clean-up on deactivated silica gel containing 2% of water. The clean-up scheme applied in the present study ensured procedural recoveries for analytes of interest in the range of 80-110% and the repeatability (RSDs) was in the range of 2-9%. The i-LOQs ranged from <1 pg for the low brominated aromatic compounds to <5 pg injected on-column for the least sensitive
detection of chlorinated aromatic compounds (Table 2). No signal saturation was found under the selected instrumental conditions with the accumulation time range from 0.025 to 0.30s, providing mass accuracy for the ions of interest below 5 ppm, and a practically linear relationship was achieved between instrumental response for the analyte ions and the accumulation time. Due to the unavailability of isotopically labelled surrogates for several analytes, matrix-matched standard calibration was used for the quantification of those compounds. Linearity with correlation coefficients of ≥0.99 was observed for all components between the i-LOQ and 250 pg injected on-column. So, once again, GC-MS is proved to be an excellent powerful technique, ensuring the highest resolving power (>1,000,000) with remarkable mass accuracy (<100 ppb), allowing for baseline resolution of closely spaced isobaric species and significantly improves the selectivity in the analysis of the questioned complex matrices in this research. Furthermore, the optimised method ensured detection sensitivity for target compounds down to picogramme amounts, which is comparable to their potential occurrence levels in water sources and also complies with the criteria set in the European Commission recommendation 2014/118/EU. Consequently, the validation results revealed that this elaborated methodology provided acceptable reproducibility, linearity, and sensitivity for the analysis of selected POPs in water samples with high fat content. In addition, the method presented is highly selective, rapid, and for the majority of compounds meets the sensitivity requirements stated in the Commission Recommendation 2014/118/EU.

Table 2. Performance Characteristics of the Method (83 Compounds; Sample Size (N)=20, Repetition (n)=5)

| Compound             | Method linearity, $R^2$ | Equation                  | i-LOQ, pg on-column | m-LOQ, ng g$^{-1}$ w.w. | Rep., % | Rec., % |
|----------------------|-------------------------|---------------------------|---------------------|------------------------|---------|---------|
| n-Decane             | 0.998                   | $y = 0.0098x - 0.0581$    | 1.0                 | 0.001                  | 4       | 83      |
| n-Dodecane           | 0.997                   | $y = 0.0102x - 0.0274$    | 1.2                 | 0.002                  | 5       | 81      |
| n-Octadecane         | 0.997                   | $y = 0.0138x - 0.0359$    | 1.3                 | 0.004                  | 6       | 80      |
| Naphthalene          | 0.998                   | $y = 0.0072x - 0.0566$    | 1.1                 | 0.001                  | 5       | 81      |
| Styrene              | 0.997                   | $y = 0.0094x - 0.0703$    | 1.2                 | 0.008                  | 3       | 80      |
| Terphenyl            | 0.998                   | $y = 0.0127x - 0.0904$    | 1.2                 | 0.004                  | 5       | 84      |
| Propoxyphenol        | 0.999                   | $y = 0.0149x - 0.0481$    | 1.0                 | 0.001                  | 2       | 86      |
| Dibenzylether        | 0.998                   | $y = 0.0152x - 0.0317$    | 1.3                 | 0.002                  | 4       | 83      |
| 2,6-di(tert.)butyl-p-benzoquinone | 0.997 | $y = 0.0101x + 0.1591$    | 2.6                 | 0.002                  | 4       | 83      |
| Dimethyl phthalate   | 0.997                   | $y = 0.0079x + 0.1468$    | 2.7                 | 0.010                  | 6       | 82      |

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| Compound                        | R²   | Equation                              | Slope | Intercept | p-value | Sigma | n  |
|--------------------------------|------|---------------------------------------|-------|-----------|---------|-------|----|
| Dibutyl phthalate              | 0.997| y = 0.00119x + 0.1251                 | 0.009 | 8         | 81      |       |    |
| 1,3,5-trimethylbenzene         | 0.998| y = 0.0047x + 0.0149 + 3.1           | 0.006 | 4         | 84      |       |    |
| 1, ethyl-2-methylbenzene       | 0.998| y = 0.0069x + 0.0175 + 3.2           | 0.008 | 7         | 82      |       |    |
| Caffeine                       | 0.996| y = 0.0052x + 0.0191 + 4.1           | 0.015 | 8         | 81      |       |    |
| Methylthiobenzothiazol         | 0.997| y = 0.0367x + 0.678 + 4.8            | 0.030 | 8         | 80      |       |    |
| 2,3-dimethyl-1-phenyl-pyrpyrazolon-5 | 0.996| y = 0.0367x + 0.678 + 5.0           | 0.040 | 9         | 80      |       |    |
| Dibutyl phthalate              | 0.997| y = 0.0020x + 0.3178 + 5.0           | 0.010 | 3         | 99      |       |    |
| Trichloromethane               | 0.997| y = 0.012x + 0.3498 + 1.0            | 0.001 | 2         | 101     |       |    |
| Tetrachloromethane             | 0.998| y = 0.034x + 0.3308 + 1.0            | 0.001 | 2         | 102     |       |    |
| 1,1,1-trichloroethane          | 0.998| y = 0.0945x + 1.4406 + 1.3           | 0.003 | 4         | 101     |       |    |
| 1,1,2-trichloroethane          | 0.999| y = 0.0945x + 1.4406 + 1.1           | 0.001 | 2         | 99      |       |    |
| Tetrachloroethene              | 0.998| y = 0.0945x + 1.4406 + 1.1           | 0.002 | 3         | 104     |       |    |
| Tri(2-chloroethyl)phosphate    | 0.998| y = 0.0615x + 0.8895 + 1.5           | 0.007 | 5         | 104     |       |    |
| 1-chloro-2-nitrobenzene        | 0.998| y = 0.0309x - 0.1631 + 1.4           | 0.006 | 4         | 102     |       |    |
| 1-chloro-3-nitrobenzene        | 0.998| y = 0.0284x - 0.1276 + 1.7           | 0.009 | 4         | 105     |       |    |
| 1-chloro-4-nitrobenzene        | 0.998| y = 0.0265x - 0.1829 + 2.1           | 0.010 | 5         | 105     |       |    |
| 1, 2-dichlorobenzene           | 0.999| y = 0.044x + 0.7102 + 3.7            | 0.011 | 5         | 107     |       |    |
| 1, 3-dichlorobenzene           | 0.999| y = 0.062x + 0.6821 + 3.2            | 0.009 | 4         | 104     |       |    |
| 1, 4-dichlorobenzene           | 0.999| y = 0.037x + 0.6952 + 3.3            | 0.010 | 4         | 106     |       |    |
| 1,2,3-trichlorobenzene         | 0.999| y = 0.058x + 0.6709 + 3.4            | 0.007 | 3         | 103     |       |    |
| 1,2,4-trichlorobenzene         | 0.999| y = 0.046x + 0.6710 + 3.3            | 0.008 | 3         | 103     |       |    |
| 1,3,5-trichlorobenzene         | 0.999| y = 0.051x + 0.6484 + 3.2            | 0.008 | 3         | 101     |       |    |
| 1,2,3,4-tetrachlorobenzene     | 0.999| y = 0.040x + 0.6438 + 3.5            | 0.007 | 5         | 97      |       |    |
| Hexachlorobenzene              | 0.998| y = 0.062x + 0.4111 + 4.0            | 0.018 | 7         | 106     |       |    |
| 4-chlorotoluene                | 0.997| y = 0.0138x - 0.0405 + 4.3           | 0.020 | 6         | 103     |       |    |
| 2,4-dichlorotoluene            | 0.997| y = 0.0125x - 0.0382 + 4.4           | 0.022 | 5         | 105     |       |    |
| 2,4,5-trichlorotoluene         | 0.997| y = 0.0132x - 0.0369 + 4.8           | 0.025 | 5         | 105     |       |    |
| Hexachlorobutadiene            | 0.998| y = 0.0126x + 0.0491 + 3.5           | 0.018 | 4         | 104     |       |    |
| PCB                            | 0.997| y = 0.0142x + 0.0377 + 4.4           | 0.026 | 6         | 96      |       |    |
| Bis-(2-chloroisopropyl)ether   | 0.998| y = 0.0159x + 0.0466 + 4.0           | 0.023 | 4         | 98      |       |    |
| α -HCH 65                      | 0.998| y = 0.0193x + 0.0506 + 4.6           | 0.021 | 8         | 95      |       |    |
| γ –HCH                         | 0.998| y = 0.0174x + 0.0713 + 4.5           | 0.023 | 7         | 96      |       |    |
| Chemical            | Correlation Coefficient | Regression Equation | Slope   | Intercept | R²    | p-value | p-value Corrected |
|---------------------|-------------------------|---------------------|---------|-----------|-------|---------|--------------------|
| Heptachlor          | 0.998                   | $y = 0.0208x + 0.0516$ | 4.0     | 0.020     | 5     | 98      |
| Aldrin              | 0.998                   | $y = 0.0157x + 0.0318$ | 4.4     | 0.026     | 7     | 105     |
| Dieldrin            | 0.998                   | $y = 0.0192x + 0.0599$ | 4.7     | 0.021     | 6     | 98      |
| $\alpha$-Endosulphan | 0.997                   | $y = 0.0108x + 0.0306$ | 5.0     | 0.029     | 8     | 92      |
| $\beta$-Endosulphan | 0.997                   | $y = 0.0124x + 0.0327$ | 4.8     | 0.026     | 7     | 94      |
| DDE                 | 0.998                   | $y = 0.0216x + 0.0495$ | 5.0     | 0.028     | 8     | 93      |
| o,p-DDT             | 0.997                   | $y = 0.0268x + 0.0511$ | 5.0     | 0.023     | 5     | 93      |
| p,p-DDT             | 0.997                   | $y = 0.0227x + 0.0523$ | 4.9     | 0.025     | 5     | 95      |
| DDD                 | 0.997                   | $y = 0.0285x + 0.0399$ | 5.0     | 0.028     | 8     | 92      |
| Chlorocresols       | 0.999                   | $y = 0.0116x + 0.1547$ | 3.3     | 0.020     | 4     | 97      |
| Bis(2-chloroisopropyl)ether | 0.998 | $y = 0.0183x + 0.1582$ | 2.6     | 0.014     | 3     | 99      |
| Bis(2-chloropropyl)ether | 0.998 | $y = 0.0153x + 0.1514$ | 2.5     | 0.011     | 3     | 101     |
| Di(4-chlorobutyl)ether | 0.998 | $y = 0.0177x + 0.1508$ | 2.2     | 0.009     | 3     | 103     |
| Aniline             | 0.999                   | $y = 0.0023x + 0.0116$ | 2.0     | 0.007     | 4     | 99      |
| 4-chloroaniline      | 0.999                   | $y = 0.0058x + 0.0132$ | 1.5     | 0.005     | 4     | 101     |
| 3,4-dichloroaniline  | 0.999                   | $y = 0.0064x + 0.0179$ | 1.7     | 0.008     | 6     | 104     |
| Tribromoethene       | 0.999                   | $y = 0.0322x + 0.0184$ | 4.8     | 0.025     | 7     | 105     |
| Azobenzene          | 0.996                   | $y = 0.0216x + 0.0503$ | 5.0     | 0.028     | 9     | 109     |
| 1-nitrobenzene      | 0.997                   | $y = 0.0070x + 0.0667$ | 4.6     | 0.027     | 8     | 107     |
| 2-nitroaniline      | 0.997                   | $y = 0.0086x + 0.0682$ | 4.6     | 0.022     | 6     | 105     |
| 3-nitroaniline      | 0.997                   | $y = 0.0073x + 0.0691$ | 4.9     | 0.025     | 7     | 108     |
| 4-nitroaniline      | 0.998                   | $y = 0.0076x + 0.0633$ | 4.7     | 0.024     | 8     | 106     |
| 2-nitrotoluene      | 0.997                   | $y = 0.0011x + 0.0067$ | 5.0     | 0.029     | 9     | 109     |
| 3-nitrotoluene      | 0.997                   | $y = 0.0008x + 0.0059$ | 5.0     | 0.029     | 9     | 108     |
| 4-nitrotoluene      | 0.997                   | $y = 0.0017x + 0.0072$ | 5.0     | 0.026     | 8     | 109     |
| 2,4-dinitrotoluene  | 0.996                   | $y = 0.0021x + 0.0062$ | 5.0     | 0.029     | 8     | 109     |
| Nitroanisoles       | 0.995                   | $y = 0.0044x + 0.0093$ | 5.0     | 0.031     | 9     | 95      |
| Nitronaphthalene    | 0.997                   | $y = 0.0038x + 0.0114$ | 5.0     | 0.027     | 7     | 97      |
| Nitrobenzaldehyde   | 0.997                   | $y = 0.0047x + 0.0162$ | 5.0     | 0.025     | 7     | 92      |
| Trifluoromethylaniline | 0.995 | $y = 0.0173x + 0.4108$ | 5.0     | 0.018     | 5     | 105     |
| N-4-butylbenzenesulfonamide | 0.995 | $y = 0.0199x + 0.4682$ | 5.0     | 0.013     | 5     | 106     |
| Methylpyridine      | 0.996                   | $y = 0.0307x + 0.2059$ | 4.2     | 0.015     | 4     | 103     |
| Dimethylpyridine    | 0.996                   | $y = 0.0381x + 0.2273$ | 4.4     | 0.017     | 6     | 104     |
| Benzonitrile        | 0.997                   | $y = 0.0082x + 0.0506$ | 5.0     | 0.028     | 7     | 107     |
Methylaniline  0.998  \[ y = 0.0099x + 0.0428 \]  4.2  0.022  4  106
Dimethylaniline  0.998  \[ y = 0.0071x + 0.0580 \]  4.5  0.023  5  106
N,N-dimethylaniline  0.998  \[ y = 0.0053x + 0.0715 \]  4.6  0.027  5  102
N-ethylaniline  0.997  \[ y = 0.0077x + 0.0421 \]  4.3  0.029  3  95
N-acetyl-N-ethylaniline  0.996  \[ y = 0.0111x + 0.0546 \]  5.0  0.030  9  93
N-ethyl-N-benzylaniline  0.996  \[ y = 0.0124x + 0.0483 \]  5.0  0.028  9  93
N-ethylaniline  0.996  \[ y = 0.0105x + 0.0492 \]  5.0  0.025  9  92

Rep.: Repeatability, %; Rec.: Recovery, %

3.2 Persistence of Chemicals in Ground Water and Infiltrated Surface Water in Syria

3.2.1 Ground Water

A ground water contamination by chemicals has been found indicating the group of chemical compounds which are most persistent in ground water. The study included 5 water supply systems pointed at the presence of lower chlorinated compounds such as trichloroethene (TCE, C₂HCl₃), tetrachloromethane (TCM, CCl₄), and tetrachloroethene (perchloroethene or PCE, Cl₂C=CCl₂) in various ground waters, probably due to industrial spillages of these compounds into the soil. A more extended inventory relating to all 120 ground water pumping stations of the country showed the presence of trichloromethane (chloroform, CHCl₃), tribromoethene (1, 1, 2-tribromoethylene, C₂HBr₃), trichloroethene (TCE, CICH=CCl₂), and tetrachloroethene in a number of these stations at levels sometimes considerably above 1µg/l. Also, 1, 1-dichloroethene (DCE, H₂C=CCl₂) pollution at levels varying from 1-10µg/1 were found. In addition to halogenated alkanes and alkenes also chlorinated benzenes (see: https://www.roadmaptozero.com/fileadmin/layout/media/downloads/en/Chlorobenzenes.pdf) and in particular 1, 4-dichlorobenzene (para-dichlorobenzene or p-DCB, C₆H₄Cl₂) and 1,2,4-trichlorobenzene (1,2,4-TCB, C₆H₃Cl₃) were detected at levels between 0.30-3.00µg/l in some samples (see Table 3).

| Compound                     | Maximum level detected (µg/l) |
|------------------------------|-------------------------------|
| Trichloromethane             | 5.09±0.83                     |
| 1,1,1-trichloroethene        | 0.17±0.02                     |
| Tribromoethene               | 100±11.4                      |
| Trichloroethene              | 1100±74.8                     |
| Tetrachloromethane           | 5.48±0.81                     |
| Tetrachloroethene            | 22.6±3.97                     |

Table 3. Compounds Detected in Cases of Ground Water Contamination in Barada Basin (N=50; n=3)
1,4-dichlorobenzene  3.02±0.65
1,2,4-trichlorobenzene  1.28±0.26

Although, all these compounds are relatively volatile they can be extremely persistent in ground waters, as may also be concluded from other studies (Hosomi, 1998; Kretchik, 2002). A similar preliminary case of contamination by chlorinated hydrocarbons was described by Mohamad and Lorenz (2009) in relation to ground water near Sarakeeb/Ilib (northwestern Syria). Recently, a case of severe ground water contamination by α,α,α-trifluorotoluene (C₆H₅CF₃) derivative in South Litani region in South Lebanon was discovered (Youssef et al., 2015). Levels of 100µg/l or more of 4-chloro-α,α,α-trifluorotoluene (P-chlorobenzorifluoride or CTT, C₆H₄ClF₃), 3-nitro-4-chloro-α,α,α-triﬂuorotoluene (NCTT, C₆H₅ClF₃NO₂) and 3,5-dinitro-4-chloro-α,α,α-trifluorotoluene (DNCTT, C₆H₄ClF₃N₂O₄) were found, while in the drinking water 1µg/l NCTT was detected. In the cases mentioned above extensive measures had to be taken to prevent the contamination of the drinking water derived from these sources (Liu et al., 2009).

3.2.2 Infiltrated Surface Water

As the Barada River is contaminated with a variety of industrial chemicals, the practice of infiltrating this water by means of bank filtration or dune filtration provides a unique opportunity to study the behaviour of chemicals in the subsoil. No local experiences about this subject were ever published, thus, other studies were cited here as in Greece (Katsoyiannis & Samara, 2004) and in Poland (Dmitruk et al., 2008) have shown differences between both types of infiltration as also illustrated in Table 4.

| Compound                  | Average concentration (µg/l) | Reference |
|---------------------------|-----------------------------|-----------|
|                           | Before infiltration         | After Bank filtration (ΔT=1-12 months) | Dune filtration (ΔT=2-3 months) |
| Trichloromethane          | 20                          | 6.50      | <0.1                  | Zimmermann-Dimer et al., 2009 |
|                           | 0.50-1.00           | 0.30-1.00 | 0.10                | (Duncan et al., 2017)         |
| Trichloroethylene         | 0.30-1.80            | 0.05-0.3  | 0.05                | (Penny et al., 2010)          |
| Tetrachloromethane        | 1.00                   | 1.00      | 0.10                | (Pusz et al., 2014)           |
| Hexachlorobutadiene       | 1.00                   | <0.01     | 0.03                | (Goldbach et al., 1976)       |
| 1,2-dichlorobenzene       | 0.90-1.90             | 0.80-1.10 | 0.03                | (Kurt et al., 2013)           |
| 1,2,4-trichlorobenzene    | 0.50                   | 0.30      | 0.01                | (Lee & Cody, 2001)            |
1,2,3,4-tetrachlorobenzene  0.10  0.03  0.01  (Koelmans & Luklema, 1992)
Hexachlorobenzene  0.01  0.006  <0.01  (Jiang et al., 2015)
γ-HCH  0.03  0.03  0.01  (Gupta et al., 2000)
PCB  0.08  0.04  (Aluani et al., 2016)
Bis-(2-chloroisopropyl)ether  3.00  2.00  0.30  (Manwaring et al., 1977)
Aniline  2.30  1.40  (Pierpoint et al., 2003)
4-chloroaniline  0.10  0.03-0.10  <0.01  (Vangnai et al., 2007)
3,4-dichloroaniline  0.70  0.03-0.20  <0.01  (Roehrs et al., 2012)
Nitrobenzene  0.50  <0.01  <0.01  (Yan et al., 2015)
p-nitrotoluene  0.50  <0.01  <0.01  (Ju et al., 2011)
p-nitroaniline  0.50  <0.01  <0.01  (Zhu et al., 2005)
p-chloronitrobenzene  0.30  <0.01  <0.01  (Mohadesi et al., 2017)
Trifluoromethylaniline  0.10  0.08  <0.01  (Unyimadu et al., 2017)

Generally, dune filtration results in a better removal of organic compounds. This is most dramatically found for the trihalomethanes (THMs, CHX) which show a high persistence during bank filtration, but already have been efficiently removed from the water phase by dune infiltration during the last five decades.

Possibly, a higher absorption capacity of the dune subsoil is responsible for this effect. Tetrachloromethane (Current study: 5.48µg/l; Literature: 0.05-1.80µg/l) seems to persist less than tetrachloroethene (Current study: 22.6µg/l; Literature: 0.10-1.00µg/l), but remains present at higher levels than hexachlorobutadiene (Current study: 2.00-48.0µg/l; Literature: 0.03-1.00µg/l). Dichloro- and trichlorobenzenes (Current study: 3.02µg/l and 1.28µg/l, respectively; Literature: 0.03-1.90µg/l and 0.01-0.50, respectively) were also found to be persistent, which is in accordance with the data reported for natural ground waters. Not only lindane (gamma-hexachlorocyclohexane or γ-HCH, C₆H₆Cl₆) but also bis (2-chloro-isopropyl) ether (Propane, 2,2’-oxybis (2-chloro-; Propane, 2,2’-oxybis*2-chloro-; 2,2’-oxybis (2-chloropropane) or C₆H₁₂Cl₂O) (Current study: 1.00-63.0µg/l; Literature: 0.30-3.00µg/l) and phosphates like tri (2-chloroethyl) phosphate (Current study: 1.00-63.0µg/l; Literature: 0.10-70.0µg/l) were found in practically unchanged concentrations after infiltration, contrary to a number of nitro-compounds which were all broken down during soil passage. This probably was due to reduction of the nitrogroup which might result in the formation of more toxic compounds such as chloroanilines (ClC₆H₄NH₂) (Current study: ND; Literature: <0.01-0.7µg/l) from chloronitrobenzenes (Current study: 0.30-3.2µg/l; Literature: <0.01-0.3µg/l).
3.3 Persistence of Chemicals in Rivers and Lakes in Syria

3.3.1 General Aspects
During the last two decades, the surface waters of Syria have been monitored for the presence of an increasing number of pollutants. However, only this study was considered the presence of a wide range of organic micropollutants in the Barada River.

3.3.2 Data Available from Routine Water Quality Monitoring Programs
A selection has been made of these data out of the water quality data systems for the national surface waters which would provide most meaningful estimates of the half-lives of chemical compounds in surface water in Syria. The results of the compounds and locations selected are given in Table 5.

Table 5. Estimated Half-Lives of Chemicals in Surface Waters in Case a First Order Reduction Process May be Assumed (June-September, 2007)

| Compound                          | Concentration (µg/l) | Lot I (Ain Al-Fijah) | Lot II (Zabadani) | Lot III (Mezzeh) | Lot IV (Jesrin) | Lot V (Ottaibah) |
|----------------------------------|----------------------|----------------------|-------------------|------------------|----------------|-----------------|
| **Hydrocarbons**                 |                      |                      |                   |                  |                |                 |
| 1,3,5-Trimethylbenzene           | 0.01                 | 1.03                 |                   |                  |                |                 |
| 1, ethyl-2-methylbenzene         | 0.01                 | 0.50                 |                   |                  |                |                 |
| Styrene                          | 0.01                 | 0.66                 |                   |                  |                |                 |
| Naphthalene                      | 0.03                 | 2.30                 |                   |                  |                |                 |
| Decanes                          | 0.10                 | 1.10                 |                   |                  |                |                 |
| Dodecanes                        | 0.32                 | 0.54                 |                   |                  |                |                 |
| Octadecanes                      | 0.01                 | 1.47                 |                   |                  |                |                 |
| Terphenyl                        | 0.10                 | 0.62                 |                   |                  |                |                 |
| **Oxygen Containing Compounds**  |                      |                      |                   |                  |                |                 |
| Propoxyphenol                    | 1.01                 | 1.52                 |                   |                  |                |                 |
| Dibenzylether                    | 0.30                 | 0.47                 |                   |                  |                |                 |
| 2,6-di(tert.)butyl-p-benzoquinone| 0.32                 | 3.45                 |                   |                  |                |                 |
| Dimethyl phthalate               | 0.33                 | 0.27                 |                   |                  |                |                 |
| Dibutyl phthalate                | 1.04                 | 0.49                 |                   |                  |                |                 |
| **Halogen Containing Compounds** |                      |                      |                   |                  |                |                 |
| Dichloromethane                  | 5.05                 | 33                   | 38                |                  |                |                 |
| Trichloromethane                 | 5.22                 | 1.08                 | 1.43              | 31               |                |                 |
| Tetrachloromethane               | 2.75                 | 0.44                 | 3.92              | 56               | 38             |                 |
| 1,1,2-trichloroethane            | 0.03                 | 1.95                 |                   |                  |                |                 |
| Azobenzene                       | 0.36                 | 1.42                 |                   |                  |                |                 |
| Compound                        | 1   | 2   |
|--------------------------------|-----|-----|
| 2-nitroaniline                 | 1.00| 2.37|
| 3-nitroaniline                 | 0.10| 1.03|
| 4-nitroaniline                 | 1.04| 3.81|
| Nitrobenzene                   | 1.02| 1.09|
| 2-nitrotoluene                 | 3.05| 3.21|
| 3-nitrotoluene                 | 0.38| 2.72|
| 4-nitrotoluene                 | 1.08| 2.74|
| 2,4 dinitrotoluene             | 0.35| 1.78|
| Nitroanisoles                  | 1.02| 1.30|
| Nitronaphthalene               | 0.30| 0.75|
| Nitrobenzaldehyde              | 0.32| 1.53|
| **Miscellaneous Compounds**    |     |     |
| Tri(2-chloroethyl)phosphate    | 1.05| 2.37|
| 1-chloro-2-nitrobenzene        | 1.08| 3.29|
| 1-chloro-3-nitrobenzene        | 1.03| 2.61|
| 1-chloro-4-nitrobenzene        | 0.31| 0.92|
| N-4-butylbenzenesulfonamide    | 1.04| 1.47|
| Caffeine                       | 0.18| 0.82|
| Methylthiobenzothiazol         | 0.03| 2.85|
| 2,3-dimethyl-1-phenyl-pyrazolon-5 | 1.07 | 5.50 |
| Trichloroethene                | 1.00| 1.27| 4.35| 31 |
| Tetrachloroethene              | 1.03| 9.98| 31  |
| Hexachlorobutadiene            | 2.04| 6.73| 2.24| 48 |
| Chlorobenzene                  | 0.15| 0.3 |
| 1, 2-dichlorobenzene           | 2.02| 1.29| 1.93| 37 |
| 1, 3-dichlorobenzene           | 1.26| 2.04| 0.92|   |
| 1, 4-dichlorobenzene           | 1.18| 1.15|     | 24 |
| 1,2,3-trichlorobenzene         | 0.83| 1.92|     | 30 |
| 1,2,4-trichlorobenzene         | 1.52| 2.16| 1.58| 28 |
| 1,3,5-trichlorobenzene         | 0.47|     |     | 18 |
| 4-chlorotoluene                | 0.03| 1.24|     |   |
| 2,4-dichlorotoluene            | 0.35| 1.09|     |   |
| 2,4,5-trichlorotoluene         | 0.15| 1.81|     |   |
| Hexachlorobenzene              | 0.10| 1.42| 27  | 50 |
| α -HCH 65                      | 0.05| 1.78| 65  | 77 |
| γ –HCH                         | 0.05| 10.2| 80  | 138|
| Compound                          | Concentration | Half-Life |
|----------------------------------|---------------|-----------|
| Heptachlor                       | 0.005         | 38        |
| Aldrin                           | 0.06          | 34        |
| Dieldrin                         | 0.003         | 300       |
| α-Endosulphan                    | 0.003         | 38        |
| β-Endosulphan                    | 0.002         | 45        |
| DDE                              | 0.003         | 690       |
| o,p-DDT                          | 0.003         | 110       |
| p,p-DDT                          | 0.01          | 56        |
| DDD                              | 0.004         | 45        |
| Chlorocresols                    | 0.10          | 2.00      |
| Bis(2-chloroisopropyl)ether      | 1.08          | 3.16      | 63 |
| Bis(2-chloropropyl)ether         | 1.02          | 1.68      |
| Di(4-chlorobutyl)ether           | 0.34          | 0.57      |

**Nitrogen Containing Compounds**

| Compound               | Concentration | Half-Life |
|------------------------|---------------|-----------|
| Methylpyridine         | 0.03          | 1.06      |
| Dimethylpyridine       | 0.17          | 1.32      |
| Benzonitrile           | 0.19          | 1.37      |
| Aniline                | 0.03          | 2.30      |
| Methylene                  | 0.10         | 1.04      |
| Dimethylaniline        | 0.38          | 2.05      |
| N,N-dimethylaniline     | 0.32          | 2.37      |
| N-ethylaniline         | 0.31          | 1.13      |
| N-acetyl-N-ethylaniline | 0.17          | 4.09      |
| N-ethyl-N-benzylaniline | 1.09          | 0.15      |
| Methoxyaniline         | 0.34          | 1.06      |

Along the length of the river from Ain Al-Fijah till Ottaibah no important discharges of chemicals were expected, so it was anticipated to be able to estimate the half-lives of many chemicals present at concentrations varying from 0.01-1.00µg/l under relatively controlled field conditions. It was found that this assumption was generally valid with an exception for lower aromatic hydrocarbons and organophosphates resulting from resp. oil spillages and domestic waste water discharges during the day considered.

### 3.3.2.1 Estimation of Half-Lives

Assuming that reduction of the concentration of the chemicals takes place according to a first order overall process, the corresponding reaction constant and half-lives were estimated from the observed drop in concentration during the known retention period. The half-lives presented in Table 6 will in some cases be relatively large due to introduction of the chemical by, e.g., deposition of air pollution.
The data illustrate the large difference in persistence of the chemicals in Barada River as compared to the persistence in lakes. The half-lives are mostly at least a factor 10 higher in the lakes than in the Barada River.

3.3.3 Differences in Persistence of Aquatic Pollutants and Their Causes

3.3.3.1 Classification of Compounds according to Differences in Persistence

Based on the data presented in Tables 4 and 5, a classification of organic compounds according to their persistence in different aquatic environments is proposed as given in Table 6. This Table shows the large differences in half-lives which can occur in different aquatic environments. The persistence of many organic compounds will be 100 times higher in ground water than in river water, while the persistence of a compound in lake water will have an intermediate value. The first category of compounds showing the lowest persistence in water can be characterised as the group of substances which are readily hydrolysed or biodegraded in both aerobic and anaerobic environments. Their half-lives range from about 1 hour in river water till 1 day in ground water.

### Table 6. Categorisation of Aquatic Pollutants According to Their Persistence in Water (June 2007-August 2008)

| Item | Compound                | Estimated half-life in water (days) |
|------|-------------------------|-------------------------------------|
|      |                         | <0.3  | 0.3-3.0 | 3.0-30 | 30-300 | ≥300 |
| i    | Dimethylphthalate       | R     |         |        |        |      |
| ii   | Nitrobenzene            | R     |         |        |        |      |
|      | 1,4-chloronitrobenzene  | R     | G       |        |        |      |
|      | Propoxyphenol           | R     |         |        |        |      |
|      | Dibenzylether           | R     |         |        |        |      |
|      | Methoxyaniline          | R     |         |        |        |      |
| iii  | Aniline                 | R     | R       |        |        |      |
|      | 4-chloroaniline         | R     | R       |        |        |      |
|      | Octadecane              | R     | R       |        |        |      |
|      | Trichloromethane        | R     | L       | R       |        |      |
|      | 1,2-dichlorobenzene     | R     | L       | R       |        |      |
|      | 1,2,4-trichlorobenzene  | R     | L       | R       |        |      |
| Iv   | Tetrachloromethane      | R     |         |        |        | LG   |
|      | Hexachlorobenzene       | R     |         |        |        | LG   |
|      | Tetrachloroethene       | R     |         |        |        | LG   |
|      | Hexachlorobutadiene     | R     |         |        |        | LG   |
|      | Bis(2-chloroisopropyl)ether | R |         |        |        | LG   |
|      | β-Endosulphan           |       |         |        |        |      |
The second category of slightly persistent compounds includes substances which are still rapidly biodegradable both aerobically and anaerobically and often contain oxygen in their molecules. *The half-life varies from about 1 day in river water till 10 days in ground water.*

The third category of moderately persistent compounds can still be rapidly reduced in concentration by aerobic biological degradation or volatilisation, but these compounds show increased resistance to removal in anaerobic circumstances or in cases where volatilisation cannot take place. *The half-life*
ranges from 1 day in rivers till 10 days in lakes and 100 days in ground waters.

The fourth category of persistent substances consists of compounds which are more difficult to degrade both in surface waters and in ground waters with half-lives ranging from 3-10 days in rivers till 100 days in lakes and ground waters.

Finally, the fifth category of very persistent aquatic pollutants consists of relatively non-volatile and non-biodegradable compounds showing half-lives of more than 100 days in lakes and ground waters.

Possible causes of differences in persistence as indicated by laboratory testing, it may be expected that degradation of a compound due to biological processes will generally result in half-lives of one or more days (Bengtsson, 2002; Magulova & Priceputu, 2016). This falls well within the range found for the situation of the Barada River in Syria. Evaporation rates calculated from equilibrium thermodynamics considerations (Li & Goel, 2012) show, however, much lower half-lives, ranging from a few seconds for alkanes like \( n \)-octane till 30 minutes for benzene, toluene and xylene and a few hours for naphthalene and biphenyl. Evaporation rates measured by laboratory testing (Nagata & Tamura, 1983; Ince, 1992; Koper & Klabunde, 1997; Kleiman & Prinn, 2000) also show low half-lives of 15-45 minutes for compounds such as chloroform, tetrachloromethane, and tetrachloroethene.

It must be concluded that volatilisation plays a much less pronounced role under field conditions than may be expected from simple laboratory testing. Apparently, a large resistance exists in practice to reach the equilibrium state. Similar findings have been reported in relation to hydrolysis and microbial breakdown of malathion (organophosphate insecticide, \( \text{O}_2\text{O}-\text{dimethyl dithiophosphate of diethyl mercaptosuccinate, C}_{10}\text{H}_{19}\text{O}_6\text{PS}_2 \)) which took place at a lower rate in an environmental simulator than the rates measured in laboratory studies (Mahanta, 2016; Walia et al., 2018).

As the half-lives of chemicals in water are considerably longer in stagnant surface waters, it may be assumed that turbulence is a major factor with regard to the persistence of chemicals in surface waters.

Turbulence increases volatilisation as well as biodegradation, but may also contribute to a more rapid photochemical degradation both by propagating sensitised photolysis and by more frequently exposing all water particles to the sunlight near the water surfaces. The increased half-lives in ground water can be attributed primarily to prevention of volatilisation and the occurrence of anaerobic conditions.

Adsorption processes (Aljerf & Choukaife, 2015), however, will play a much more pronounced role. But the increased adsorption might be largely compensated by the effect of the absence of turbulence, resulting in minimum half-lives which are somewhat above those in rivers, even for non-volatile biodegradable compounds.

4. Conclusions

Estimates from laboratory testing of the most important route of removal of an aquatic pollutant may result in a too optimistic prognosis for the persistence of a pollutant in surface water. Experiments under conditions prevailing in water bodies with long retention times are essential to overcome this problem and to be able to develop a sound theoretical basis for the extrapolation from simple laboratory
tests to the field. Although, a great need exists to restrict oneself to simple and reproducible laboratory tests in order to obtain data for many compounds in the shortest time, it must be realised that it will not be fully acceptable to do so until a theoretical framework has been developed which allows for a reliable extrapolation to the field conditions considered. Therefore, it is recommended to pay much more attention at short notice to field experiments than has been done so far. Many data on the occurrence of chemical compounds in the aquatic environment have already been collected and should be used in this context as illustrated in this paper. It would be wasteful not to use them as much as possible. Only after locally valid data are available, a chemical compound should be classified as being persistent or not.

Based on the classification given in Table 6, it is proposed that in the context of international conventions against the pollution of the aquatic environment those compounds are considered to be persistent which show half-lives above 30 days in one or more water compartments which are relevant for the local situation. Such a basis would extend the list of compounds to be controlled with high priority and is considered to be essential for the protection of not only the organisms living in rivers, but also of those depending on the water quality in lakes and in the subsoil.

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