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Review

# Storage of natural water samples and preservation techniques for pharmaceutical quantification

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ABSTRACT

In order to perform a human and ecological risk assessment of pharmaceutical products (PPs) in natural waters, it is necessary to accurately quantify a broad variety of PPs at low concentrations. Although numerous currently implemented analytical methodologies, less is known about the preservation of PPs in natural water samples within the period before analysis (holding time, storage conditions). This paper is the first literature review about the stability of PPs in natural waters (surface and groundwaters) during sample storage. The current work focuses on a comparison of the performances of the available preservation techniques (filtration, container materials, storage temperature, preservative agents, etc.) for PPs in samples. All 58 reviewed PPs may be successfully stabilized during 7 days in surface waters by at least one appropriate methodology regarding temperature, acidic and non-acidic preservatives. When temperature is not a sufficient preservation parameter for some PPs (hormones and fluoxetine) its combination with the addition of chemical agents into the samples may prolong the integrity of the PPs during storage in surface water. There is a strong need to use standard protocols to assess and compare the stability of PPs in environmental water matrices during storage as well as during analytical preparation or analysis (European criteria 2002/657/EC). Since the stability of PPs during sample storage is a critical parameter that could call into question the quality of the data provided for the concentrations, the design of stability studies should rigorously take into account all critical parameters that could impact the concentrations of the PPs with time.



**Contents**



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## 1. Introduction

In recent decades, the presence of Pharmaceutical Products (PPs) (human or veterinary) in natural waters has increasingly raised worldwide concerns (public, scientists, and regulators) about their possible risks for aquatic fauna and flora as well as for human beings. There are a myriad of PP contamination sources in the aquatic environment as described in the literature [1–3]. However, the major contamination pathways for human and veterinary PPs to enter into water bodies are respectively from household wastewater effluents and their soil transfer after soil amendment by biosolids and liquid waste from treated animals. A PP is a bioactive compound that may occur in the water cycle not only in its initial form (i.e. ingested and then excreted in parent form), but also as its metabolites, and/or transformation products produced in the environment and during wastewater and raw drinking water treatment processes (via abiotic and biodegradations). A broad variety of PPs (parent and transformation products) have been widely detected, albeit at low concentrations (i.e. ng/L), in surface waters, groundwaters and stream waters all over the world [4–12]. Within the EU Water Framework Directive, it has recently been proposed to add three pharmaceutical substances, i.e. 17α-ethinyloestradiol, 17β-oestradiol (E2), and diclofenac, to the list of 33 pollutants regulated in EU waters [13]. In order to examine the potential risk of PP contamination for animals and humans, it is necessary, among other tasks, to assess and monitor the release of PPs to the aquatic environment.

There is a considerable commitment to this issue thanks to the broad analytical development and implementation of new advanced methodologies that allow the identification and quantification of PPs in natural waters up to low ng/L range. In addition, efforts are currently being undertaken to implement new standard methodologies at the national scale to monitor the concentrations of PPs in natural waters [14,15]. Surprisingly, only a few studies have dealt with the stability and preservation of samples containing PPs although numerous works have published information on the performance of developed analytical methodologies and many occurrence data are reported in the literature [16–20]. Because one prerequisite of research is the accurate estimation of real concentrations of PPs in water matrices, questions arise as to how long and how to store and preserve PPs in natural water samples so that they are not depleted before analysis. Ideally, sampling and sample analysis should be carried out within one day to avoid the stability issue of PPs. Nevertheless, there are often logistical hindrances that oblige environmental laboratories to store water samples for a longer period of time before their analysis.

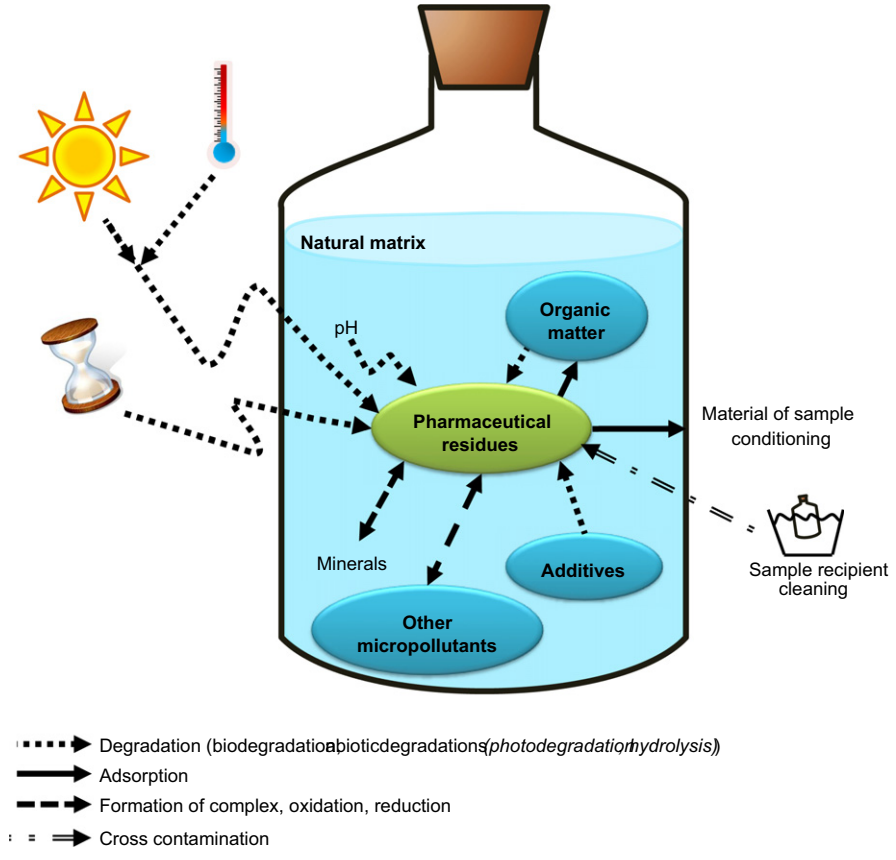


**Fig. 1.** Sources and processes (possibly) affecting the stability of PPs in samples before analysis.