



The fate of selected pharmaceuticals in solar stills: Transfer, thermal degradation or photolysis?



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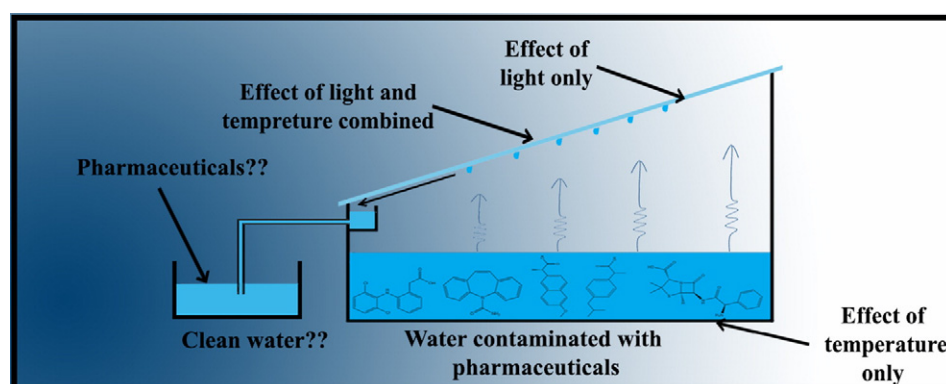
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HIGHLIGHTS

- Solar stills are highly effective in removing several pharmaceuticals.
- Single pharmaceutical (Ibuprofen) transferred into the distillate and transfer percentage was very low.
- Naproxen, Ibuprofen and Carbamazepine require the effect of light and temperature combined to degrade significantly.
- Concentrated solar power showed promising results in the degradation of several pharmaceuticals.

GRAPHICAL ABSTRACT



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ABSTRACT

The increase in demand for, and disposal of, pharmaceuticals, positively correlated with the growing human population, has led to the emergence of contaminants with high environmental and health impacts. Several developing countries that endure problems related to water sufficiency and/or quality resort to the use solar stills as an affordable water treatment method. This research is aimed at investigating the fate of five chemically distinct pharmaceuticals that might pervade solar stills; ibuprofen (IBU), diclofenac (DCF), carbamazepine (CBZ), ampicillin (AMP) and naproxen (NPX). The experiments were conducted under three conditions. The first condition studied the combined effect of temperature and light in simulated field-test-scale solar stills. The effect of temperature as a sole variable was investigated in the second while the third condition studied the effect of light only via concentrated solar power (CSP). Results show that distillates from solar stills did not contain the parent compounds for four out of the five pharmaceuticals. IBU was the only pharmaceutical that showed a transfer via vapor into the distillate with the highest recorded transfer percentage of 2.1% at 50 °C when subjected to temperature alone and 0.6% under the combined effect of temperature and light. In the case of NPX and DCF, the parent compounds did not undergo transfer into the distillate phase; however their degradation by-products did. In addition, the results also showed that in the case of NPX, IBU and CBZ both high temperatures and sunlight combined were required to attain noticeable degradation. CSP accelerated the degradation of DCF, NPX and IBU with a three-minutes-degradation percentage of 44%, 13% and 2% respectively.

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1. Introduction

Fresh water resources are becoming increasingly critical in several regions around the world (Oelkers et al., 2011). More than a billion people, the vast majority of whom reside in Asia and Africa, do not have access to clean and reliable water supplies (Water, 2012).

Solar stills are a solar based desalination/water treatment technology and are considered as one of the simplest, cheapest and most sustainable processes. However they suffer from two disadvantages: their productivity is very low compared to other desalination methods and, they require relatively large areas of land which invariably increases their initial investment (Kannan et al., 2014; Kulkarni and Kulkarni, 2014; Velmurugan and Srithar, 2011).

Nevertheless, the simple construction of solar stills and their utility in removing various contaminants, lowering salinity, and disinfecting saline and contaminated water have enhanced their use in a number of developing countries as a primary source for domestic water supply (Bhattacharyya, 2013).

Pharmaceutically active compounds (and their metabolites) occur ubiquitously in all water bodies throughout the world (Hughes et al., 2012). Trace pharmaceutical compounds have been found in surface water (Petrie et al., 2015), ground water (Phillips et al., 2015) and coastal seawater (Gaw et al., 2014) ranging in magnitude from a few ng/L in seawater and potable water to high µg/L in sewage treatment plant (STP) effluents (Arnold et al., 2014; Fick et al., 2009; Giri et al., 2014; Cardoso et al., 2014). Pharmaceuticals are released to the aquatic environment via several pathways; these include emissions from manufacturing facilities, the discharge of treated sewage effluent from sewage treatment plants, from the application of sewage sludge, or animal manure, to land, leakage from sewage treatment plants, emissions from medical units and disposal of unwanted pharmaceuticals (Kookana et al., 2014).

The partial removal of pharmaceutical compounds by conventional wastewater treatment plants has, invariably, resulted in their accumulation in the water cycle (Fick et al., 2009; Triebkorn et al., 2014), and hence their continuous release into water bodies exerts a hazardous impact on both the environment and human health (Arnold et al., 2014; Giri et al., 2014; Cardoso et al., 2014; Triebkorn et al., 2014; Whitacre, 2010). Although several treatment methods, whether physical, chemical and/or biological, have been proposed for combatting pharmaceutical contamination (Kitsiou et al., 2014), photodegradation is one of the few available methods that could utilize renewable energy and may be deployed on a large scale. Sunlight may be directly absorbed by the pharmaceutical molecule or it can produce in-solution highly oxidative products such as reactive oxygen species (ROS) (Chong et al., 2010), which in turn would react with the molecule and break it into smaller ones, eventually mineralizing it into carbon dioxide, H₂O and mineral salts (Ikehata and El-Din, 2006). Considerable research investigated both indirect photolysis and photocatalysis as methods for elimination of pharmaceuticals in water (Doll and Frimmel, 2003; Dimitrakopoulou et al., 2012; Radjenović et al., 2009).

A study by Ayoub et al. (Ayoub et al., 2014; Ayoub et al., 2015) conducted to assess the efficiency of solar stills in removing contaminants and enhancing productivity reported the possibility of bacterial transfer from the solution via vapor to the distillate. This raises the possibility of the transfer of pharmaceuticals if present in the feed water to the distillate of solar stills and the possibility of degradation due to the effect of heat and light. Each of these two factors can have a separate effect or possibly have a combined synergistic effect. Indeed, most pharmaceuticals are designed to be thermally stable, however, they are known to be light sensitive (Doll and Frimmel, 2003) and will undergo photodegradation.

There are two types of photo-degradation: direct effect, where sunlight affects the molecule directly and is often referred to as direct photolysis, or when sunlight indirectly affects the molecule. Indirect photodegradation could occur either through indirect photolysis or through

photo-catalysis (Doll and Frimmel, 2003). Considerable research effort has been expended on the utilization of indirect photolysis, photocatalysis and direct photolysis for the elimination of pharmaceuticals in water (Doll and Frimmel, 2003; Dimitrakopoulou et al., 2012; Fatta-Kassinos et al., 2011; Barnaby, 2009; Boreen et al., 2003; Mathon et al., 2016).

Experimental results reported in the literature on the recalcitrance of a particular pharmaceutical to photolytic degradation, on the number of photo degradation by products, on the mechanisms involved in the degradation process and on the toxicity of these photo degradation products for the same pharmaceutical are often contradictory. For example, Hanamoto et al., 2014 reported that photolysis of DCF did not appear to release degradation byproducts that were more toxic than the parent compound. On the other hand, Diniz et al., 2015 (Diniz et al., 2015), reported that the photolysis by-products of DCF were more toxic than the parent compound. More recently Kovacic et al., 2016 (Kovacic et al., 2016) has shown that direct photolysis of DCF resulted in the majority of the parent compound transforming into two degradation by-products and that the toxicity level of these by-products was rather low. Mathon et al., 2016 (Mathon et al., 2016) also reported on the number of photo degradation products where they reported the number to range from 1 by-product up to 13.

The main objectives of this study are to determine whether solar stills are capable of eliminating/mineralizing pharmaceuticals, whether pharmaceuticals and/or their degradation products are transferred to the distillate, thus rendering the distillate unsafe for use, and to establish which one of the mechanisms (thermal or direct photolysis) is prevalent/dominant in the degradation of pharmaceuticals or if the two mechanisms are synergistic in nature.

To achieve these objectives, the effects of light and heat, individually and in combination, on the transfer and degradation of pharmaceuticals, in the absence of mechanical disturbances, were evaluated under three different experimental modes: (a) solar still mode executed in a simulated solar still that was subjected to natural sunlight accompanied by a raise in temperature. In this mode, the synergetic effect of two independent variables, heat and ultraviolet radiation, was assessed. (b) Thermal-only mode performed in a heated container which was isolated from all light sources. This mode was set up in such a way so that heat would be the only effective variable. (c) Light-only mode implemented by a solar collector and a concentrator by which solar radiation was amplified. The duration of concentrated sunlight exposure was short in order to reduce heating of the samples.

2. Materials and methods

2.1. Pharmaceuticals used

The pharmaceuticals selected are ibuprofen (IBU), diclofenac (DCF), carbamazepine (CBZ), ampicillin (AMP), and naproxen (NPX). The selection of these five was based on their common usage, recalcitrance, potential detrimental environmental and health impacts and their identification as priority compounds in the developing world (Mansour et al., 2016).

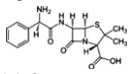


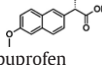
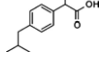
IBU was supplied from Mediphar Laboratories (Lebanon), DCF, AMP and CBZ were acquired from Mephico S.A.L (Lebanon), while NPX sodium was obtained from Al-Hikma Pharmaceuticals (Jordan). All pharmaceuticals had a purity of 99%. Characteristics of the different pharmaceuticals used in this study are presented in Table 1.

Methanol and Acetonitrile of HPLC grade were obtained from Sigma-Aldrich (Germany). Double distilled as well as deionized (DI) water (Milli-Q purification system) were used in this study.

2.2. Chemical analysis

The concentration of pharmaceuticals in solution was determined using High Performance Liquid Chromatography (HPLC), Agilent 1100

Table 1
Pharmaceuticals tested and their characteristics.

Name and structure	Chemical formula	Class	Function	Toxicity level	Henry's constant*
 Ampicillin	C ₁₆ H ₁₈ N ₃ NaO ₄ S (Kanakaraju, 2013)	Antibiotic (Packer et al., 2003)	Treats bacterial infections (Packer et al., 2003)	Hazardous upon inhalation and ingestion (Kanakaraju, 2013)	2.39 × 10 ⁻¹⁷ (Felis et al., 2007)
 Diclofenac	C ₁₄ H ₁₀ C ₁₂ NO ₂ (Ma et al., 2014)	Nonsteroidal anti-inflammatory drug (NSAID) (Oppenländer, 2003)	Has inflammation, pain and fever reduction properties (Oppenländer, 2003)	Its oral lethal dose (LD(50)) is 53 mg/kg in rats and 157 mg/kg in rabbits (Ma et al., 2014)	4.73 × 10 ⁻¹² (Hanamoto et al., 2014)
 Carbamazepine	C ₁₅ H ₁₂ N ₂ O (Boscá et al., 2001)	Anticonvulsant (Packer et al., 2003)	Used to treat seizures (Packer et al., 2003)	Hazardous upon ingestion (Boscá et al., 2001)	1.08 × 10 ⁻¹⁰ (Hanamoto et al., 2014)
 Naproxen	C ₁₄ H ₁₄ O ₃ (Arany et al., 2013)	NSAID (Oppenländer, 2003)	Alleviation of mild to moderate pain, fever, and inflammation (Oppenländer, 2003)	Oral LD(50) is 248 mg/kg in rats and 360 mg/kg in mice (Arany et al., 2013)	3.39 × 10 ⁻¹⁰ (Hanamoto et al., 2014)
 Ibuprofen	C ₁₃ H ₁₈ O ₂ (Marotta et al., 2013)	NSAID (Oppenländer, 2003)	Reduces moderate pain, fever, and inflammation (Oppenländer, 2003)	Oral lethal dose 50 (LD(50)) = 636 mg/kg in rats and 495 mg/kg in guinea pigs. Considered very hazardous (Marotta et al., 2013)	1.52 × 10 ⁻⁷ (Hanamoto et al., 2014)

* The unit for Henry's constant is atm·m³ mol⁻¹.

Series LC system, equipped with a quaternary pump, autosampler, diode array detector (DAD) and supported by an analytical work station supplied by Agilent Technologies, California USA. The separation was achieved on an analytical column Discovery C18 (5 mm, 25 cm long × 4.6 mm ID) connected to a security guard column Discovery HS C18 (5 mm, 2 cm long × 4.0 mm ID), both supplied by Supelco Sigma-Aldrich, Missouri USA. Each pharmaceutical was to be tested following a specific method summarized in Table S1 of the supplementary material. Most of these methods, though adopted from previously reported studies, were used to achieve experimentally valid results (**Table S1 of the supplementary material**).

2.3. Experimental setup

A schematic diagram for the experimental set-up along with photographic images is shown in Fig. 1.

2.3.1. Solar still mode

The solar still used in this study was composed of a closed spherical glass flask, encasing a feed plate to contain the initial solution and a support plate on which the feed plate is located at the bottom center of the glass flask. The setup of a unit solar still is shown in (Fig. 1a).

The still flask, acquired from a local supplier and customized at the AUB glass workshop, was specifically made of glass so as to prevent any chemical interactions between the pharmaceuticals and the flask. The flask is composed of a 50 L semi-spherical bowl with a flat bottom with an area of 0.13 m² and a maximum diameter of 50 cm at its mid-depth. The top opening of the flask was covered using an air-tight semi-spherical glass lid, thus completing the spherical shape of the flask. Using the method proposed by Noteboom and Will (Noteboom and Will, 1982), both parts were completely siliconized using Dichlorodimethylsilane solution purchased from Sigma-Aldrich, (Missouri, USA). The feed plate which consisted of a shallow pan made of aluminum (16 cm diameter, 2 cm deep with a maximum liquid capacity of 500 mL) had its surface coated with Teflon and its bottom with ceramic enamel. Before each experiment, the flask and the plate were washed using lab-grade detergent, followed by rinsing with distilled water, and acetone. The flask and plate were placed either in an oven at 200 °C for 2 h or left in the sunlight for 8 h in order to remove any organic residues. Prior to adding the test solution, the plate was properly leveled on the siliconized porcelain plate-support, which underwent the same washing procedure as that of the flask and the feed plate. After washing, it was placed in an oven at 200 °C for 2 h.

2.3.2. Thermal-only mode

In this mode a deep semi-spherical aluminum (34 cm diameter, 10 cm deep and a total capacity of 4 L) pan was used. Ceramic enamel and Teflon coatings were used at the bottom and the surface of the pan, respectively. The setup is displayed in (Fig. 1b).

The testing procedure included the application of one liter of the initial feed solution to the pan while a siliconized porcelain plate was centered inside the pan to function as the distillate-collector. The pan's cover was a semi-spherical siliconized glass dome. In this setup, the pan cover was placed in an inverted mode so that the concavity of the cover would direct condensate droplets towards the inside of the porcelain collection plate.

Heating was performed by placing the pan on a 500 mL Electromantle Heating Mantle EM0500, OSA (UK). The heater was connected to a programmable, temperature-controlled circuit-breaker needed to control the temperature at a preset range. For this test mode, the experiments were carried out at temperatures of 40, 50, and 60 °C. For each experimental run, the regular washing process was adopted and the temperatures of the feed, the air inside and the air outside of the pan were continuously recorded.

2.3.3. Light-only mode

In this mode, the feed solution was subjected to concentrated sunlight and ultraviolet radiation. The clarity of the feed solution (turbidity was non-detectable at 0.001 NTU on a Hach 2100AN IS turbidimeter, Loveland USA) limited the amount of light absorbed. Thus, the water temperature during these experiments did not increase when compared to the other experimental modes. However, the feed solution was exposed to significantly higher amounts of ultraviolet radiation compared to the other experimental modes. The initial feed solution was placed in a 12 mL screw-cap, clear borosilicate cylindrical vials. This vial had a radius of 1 cm, a length of 7 cm and glass-thickness of 1 mm. The vial was subjected to concentrated solar irradiation using a solar concentrator. The full setup can be seen in (Fig. 1c).

The solar concentrator, made of a standard satellite dish, was covered with two layers of reflective chrome plated sticking tape. The double layer of chrome tape had a reflectiveness value of 80%. The dish had a total area of 0.71 m², elliptical shape with major diameter of 100 cm, a minor diameter of 90 cm and a depth of 10 cm at the center. The focused image had an area of 0.0092 m² with the light intensity at the focal point equal to 76 × 0.8–62 times the power of regular sunlight. The dish was mounted on a bi-axial mount that enabled it to be directed

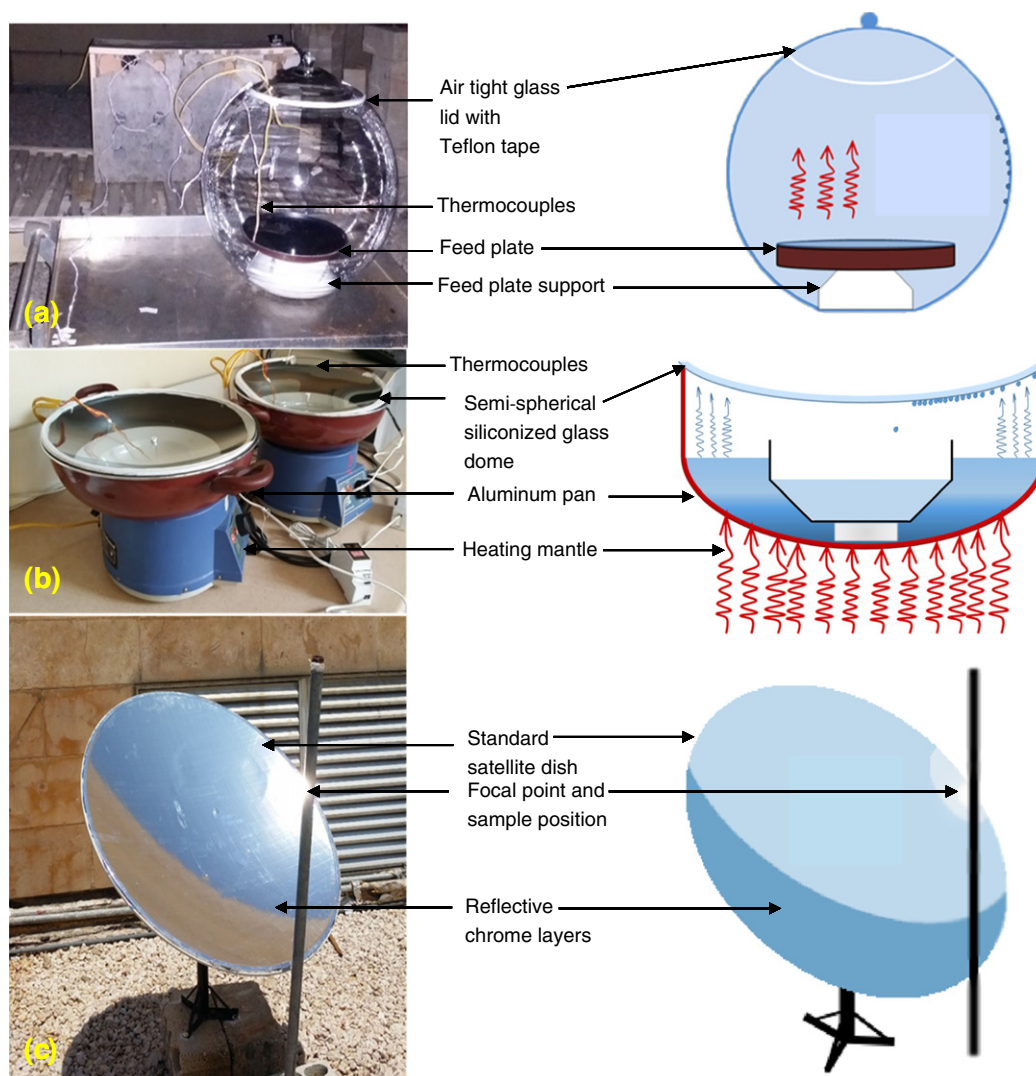


Fig. 1. Schematic and photo of experimental setups (a) solar still mode, (b) thermal only mode and (c) light-only mode.

perpendicularly to incoming solar radiation. Both natural and concentrated solar flux as well as both natural and concentrated ultraviolet radiation A and B were measured and recorded, however readings for both parameters for concentrated sunlight were over range. The temperature of the feed solution was also measured and recorded before and after each experiment. The time of exposure in this experiment was limited to 3 min under CSP and 2 h under regular sunlight and the temperature of the solution did not rise above 2 °C in both cases. The duration of exposure was varied between no exposure, regular sunlight for 2 h and concentrated sunlight for periods of 30, 60, 90, and 180 s.

2.3.4. Sensors

Temperature sensors in the form of thermocouples and thermometers and light sensors in form of lux and ultraviolet meters were used to monitor the experimental parameters. The temperature sensors included type-K thermocouples connected to 18200-00- Cole-Parmer data-acquisition system (Chicago USA) that was in turn connected to a computer. Temperature logs were obtained using Cole-Parmer TracerDAQ software (Chicago USA). The sampling frequency was set to one measurement per second.

The light sensor included a real time data logger hand-held lux meter model: LX-1128 SD with the maximum reading limit of 100,000 LUX supplied by Lutron (Taipei Taiwan). This sensor was used to measure the intensity of natural sunlight, the intensity of light absorbed by

the glass in the still and the intensity of concentrated sunlight. The meter had data-logging property, which during the solar still mode, was set to record light flux at a frequency of one measurement per second. Two different instruments were used to measure ultraviolet radiation. The first instrument was a hand-held UV meter with two sensors; one for UVA and the other for UVB. The meter, model RM-11, was supplied by Opsytec Dr. Gröbel GmbH (Germany) and had a measurement range between 0 and 20 $\text{mW} \cdot \text{cm}^{-2}$ for both UVA and UVB. The second instrument consisted of two UV-sensor chips (model number ML8511) supplied by SparkFun (Colorado USA). The function of the chips was to convert UVA and UVB into electrical potential proportional to UV intensity. The chips were connected to a NI USB-6008 a bus-powered multifunction DAQ USB device supplied by National Instruments (Austin USA). The data-acquisition unit measured the electrical potential supplied by the chips and logged it as raw data into a computer. Data was integrated and converted into UV-intensity values using custom-programmed software. NI LabVIEW was used as a program platform. Of the two sensors, one was mounted inside the still, parallel to the feed plate and the second outside the still, parallel to the flat-base of the still.

2.4. Methodology

The research aimed to study each pharmaceutical compound in distinct experimental runs. These were performed over a six-month

period. The experimental run was initiated by preparing a stock solution of the pharmaceutical. The solution was tested using HPLC and a known standard to confirm the purity and the concentration of the solution and was stored in a refrigerator at 4 °C for a maximum period of one week. This solution preparation method was common to all experimental runs.

For the thermal-only mode, each pan was filled with 1 L of the stock solution followed by positioning the distillate collector plate at the center of the pan. The pan was then sealed with a glass cover with the top sheathed in aluminum foil on the exterior. The glass cover had a hole through which two thermocouples were inserted. One was dipped into the solution while the other was positioned in the air space of the pan. At each distinct test, the temperature was kept constant at 40, 50 or 60 °C. Additionally, a third thermocouple, intended to measure the ambient temperature, was placed in the vicinity of the experimental setup. The experiment was done in duplicate using two separate pans and was timed to end at $t = 24$ h. At the end of the experiment, two samples of 2 mL were collected, one sample from the distillate and the other from the residual and the total volumes of the distillate and the residual were measured.

For the solar-still mode, the experiment was performed on the roof of the CCC-Scientific Research Building at the American University of Beirut (Latitude: N33°54'; Longitude: 35°29'; Altitude: 29 m). The glass flask was positioned and leveled on a stainless steel platform. The feed plate and the plate support were also positioned and leveled in the center of the bottom of the glass flask. The feed plate was filled with 500 mL of the stock solution. After filling the plate, time was set to $t_0 = 0$, which was always after sunset. Similar to the thermal-only mode, three thermocouples were deployed. These were used to measure the temperatures of the solution, the air inside the flask and the ambient temperature. In addition to the thermocouples, two UV sensors were installed with one located inside the still, parallel to the feed plate, while the second was placed outside the still, parallel to the experimental setup. Monitoring UV was necessary to determine the effect of UV intensity on the degradation of selected pharmaceutical compounds. Light intensity was monitored using a data logging lux meter. The experiment ended at $t = 24$ h. Three 2-mL samples were collected, one from the distillate, a second from the residual, and the third from the condensed water droplets that accumulated on the glass cover. The third sample was taken to ascertain that no cross contamination took place. The volumes of the distillate and the residual were also recorded.

As for the light-only mode, the solar concentrator was used to simulate the light intensity and to investigate the effectiveness of amplifying the solar radiation. The concentrator was first directed towards the sun, and its focal point determined using a long holder and a black sheet. Each of the six pharmaceuticals used in this study were poured in a set of six vials. Every vial was subjected to five different sets of conditions. These conditions covered regular sunlight for 2 h and concentrated sunlight for 30, 60, 90 and 180 s. UVA, UVB and solar flux of regular and concentrated sunlight were recorded. Similar measurements were also taken behind empty vials and vials filled with deionized water. Temperature for each vial was taken at the beginning and end of the experiment to ensure that the temperature rise did not exceed 2 °C.

Preliminary experiments showed that the maximum ratio of residual to initial sample was always less than 1/3 V/V, accordingly the initial pharmaceutical solutions used in this study had chosen concentrations (Table 2) that would ensure no super-saturation in case the pharmaceutical solution was concentrated up to three times at 20 °C. Solubility tests were conducted prior to any experiment.

2.5. Data analysis

The transferred and degraded percentages for each pharmaceutical were calculated by carrying out a mass balance analysis. The volumes of the distillate and the residual of each sample were measured at the end of the experiment and these values were multiplied by their

Table 2
Solubility, limit of quantification and initial concentration of each pharmaceutical.

Name of pharmaceutical	Tested solubility in DI water at 20 °C (mg L ⁻¹)	HPLC limit of quantification (µg L ⁻¹)	Initial concentration (mg L ⁻¹)
AMP	150	50	50
DCF	150	50	50
CBZ	150	50	50
NPX	15	20	5
IBU	30	25	10

corresponding concentrations to obtain a mass value. The masses obtained were defined as: m_{initial} , m_{final} , $m_{\text{distillate}}$, and m_{residual} , with m_{initial} being the mass of pharmaceutical that was in the solution at the beginning of the experiment in the solar stills and the thermal only mode. At the end of the experiment the sum of the mass of the pharmaceutical measured in the distillate ($m_{\text{distillate}}$) and the residual (m_{residual}) was considered to be the final mass (m_{final}). The percent pharmaceutical degraded is the difference between m_{initial} and m_{final} divided by m_{initial} . On the other hand the percent pharmaceutical transferred is $m_{\text{distillate}}$ divided by m_{initial} .

3. Results and discussion

3.1. Experimental conditions

Three environmentally related parameters, which may impact the stability of the pharmaceuticals in the experimental apparatus, were monitored throughout this study, namely, temperature, solar radiation intensity, and ultraviolet radiation intensity.

The solar still mode experiments were conducted during clear and sunny days only in order to minimize variability in experimental conditions and to mimic the transfer and/or degradation when targeting the highest operating temperatures. (Fig. 2) depicts averaged temperature variations in the solar still for all of the experimental runs. This figure, which represents the temperature records of eighteen different duplicated experimental tests, shows that the entire system was subjected to an external temperature of 25 ± 1 °C during night hours. However during the day the external temperature increased to reach 30 ± 1 °C while the temperature of the air inside the still increased to 45 ± 2 °C and remained constant for a period of 5 h. This trend was also followed by the pharmaceutical solution in the feed plate.

UV records for the different experimental tests also showed low variability; Fig. 3a presents averaged UV intensity levels recorded during the individual runs for a particular pharmaceutical inside the still, while Fig. 3b presents the UV intensity levels outside of the still. The same general trend is observed in the different tests except for some short but sharp fluctuations caused by the presence of intermittent clouds. The tested solutions were subjected to UV levels rising from 0 to 3.8 mW/cm² for a period of 2 h, then UV intensity remained constant at around 3.8 mW/cm² for another 3 h, after that UV intensity decreased rapidly over a period of 40 min to reach a level of 0.8 mW/cm² followed by a slow descent to a zero value which extended over a period of about 5 h.

UV intensity levels inside the solar still reached higher levels than UV outside the solar still during early morning. This occurred despite the presence of UV-absorbing glass, and is attributable to the diffraction of sunlight caused by the spherical shape of the glass still.

(Fig. 4) shows the intensity of light outside the solar still. The meter used had a maximum measuring capacity of 100,000 Lux which explains the static (truncated curve) sunlight intensity depicted in the figure. Sunlight intensity showed little variation during different experiments, the trend observed was a sharp increase in the intensity up to 100,000 Lux for a period of 2 h, then the sunlight intensity reached an unknown value above 100,000 Lux for a period of 6 h, finally the intensity decreased over a period of 2 h to reach a value of zero Lux.

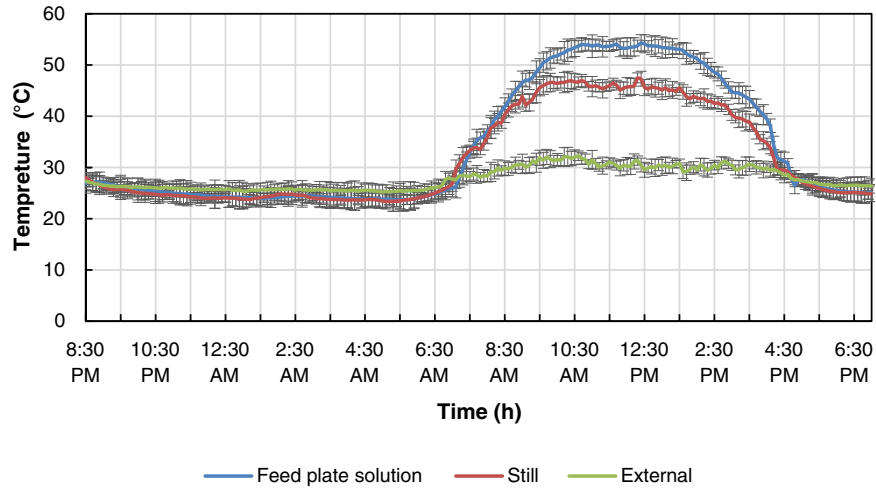


Fig. 2. Averaged temperature variation in solar still mode.

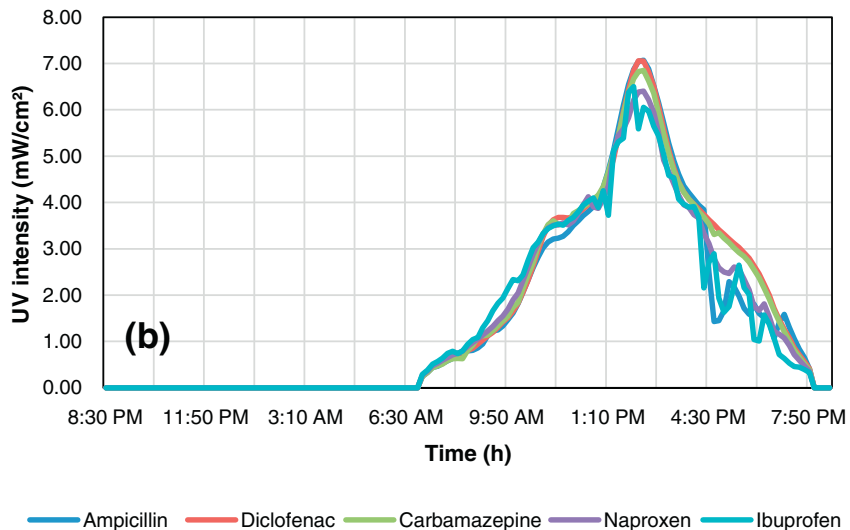
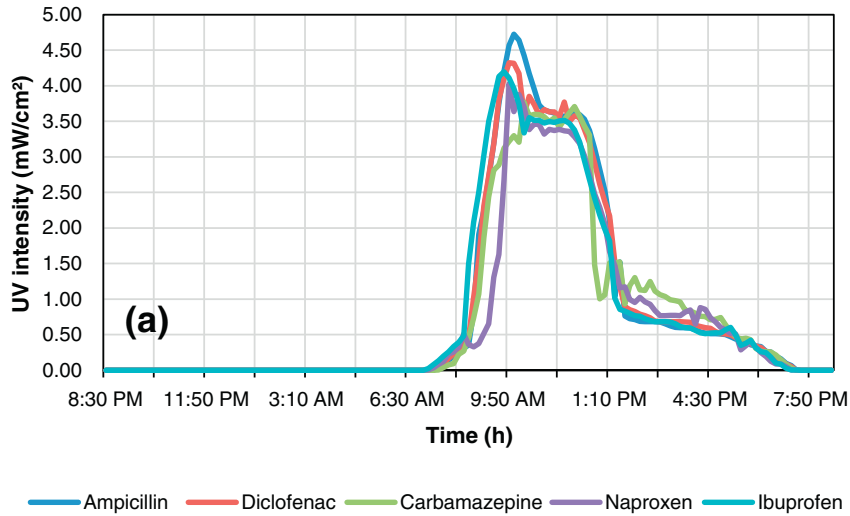


Fig. 3. Averaged UV intensity variation (a) inside the solar still for each pharmaceutical, (b) outside the solar still for each pharmaceutical.

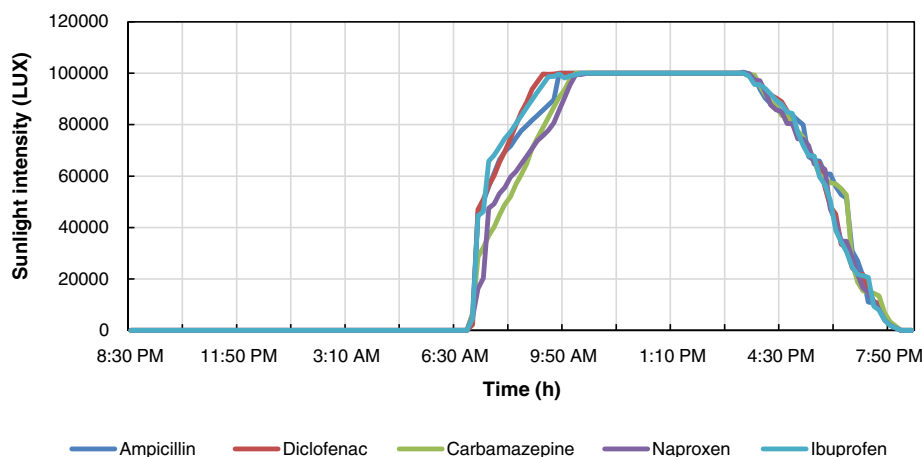


Fig. 4. Averaged sunlight intensity outside the solar still for each pharmaceutical.

3.2. Transfer and/or degradation of pharmaceuticals

Experimental results are presented in Tables 3, 4, and 5 where the percentage degradation and transfer of pharmaceuticals in the solar still thermal mode are shown in Table 3, while the degradation percentages of the pharmaceuticals under regular sunlight are shown in Table 4 and details of the presence/absence of degradation products in the distillate/residual for all modes is shown in Table 5.

3.2.1. Ampicillin (AMP)

AMP did not show significant absorbance above 290 nm, hence low direct solar degradation of the pharmaceutical was expected (Fig. 5).

In the solar still mode, AMP showed moderate degradation of about 39% (SD = 2). This observation can be attributed to the effect of temperature on the rate of degradation. No study up to date has tested AMP's fate under direct sunlight. However, two studies tested photolysis of AMP solutions exposed to artificial UV. In the first study, Lunn et al. (1994) obtained full degradation with emission in the region of 200–1400 nm (Lunn et al., 1994) while Elmolla and Chaudhuri (2009), using UV lamp that emits at 365 nm, reported insignificant degradation of AMP (Elmolla and Chaudhuri, 2009). In the current study no AMP transfer to the distillate was detected. Similarly degradation byproducts were not detected in the distillate or in the residue.

For the thermal only mode AMP showed only a 1% degradation at 40 °C, however at 50 and 60 °C the degradation rate increased to 30% and 38%, respectively. Compared with the solar still degradation results (39%), it could be assumed that AMP undergoes thermal degradation. A study done by Oliyai and Lindenbaum (1991) showed that AMP could be thermally decomposed and the observed degradation rate constant increased from 74 h⁻¹ at 25 °C to 500 h⁻¹ at 50 °C (Oliyai and

Lindenbaum, 1991). Also in thermal only mode no transfer was encountered in this study.

AMP did not show any degradation neither under concentrated sunlight nor under regular sunlight. This confirms previous observations that AMP is a very stable compound even under intensified light.

3.2.2. Diclofenac (DCF)

The absorption spectrum of DCF (Fig. 5) showed a maximum at 202 nm, tailing over and overlapping with the UV radiation of sunlight in the region of 300–330 nm.

Six tests in the solar still mode showed an average of 50% (SD = 3) degradation in the residual accompanied by the formation of a byproduct (retention time = 6.1 min) that was retained in the residual without being transferred. Another byproduct (retention time = 8.8 min) was detected only in the distillate and not in the residual indicating its affinity to vaporize directly after its formation. However, the parent compound DCF was not detected in the distillate. The observed rate of degradation of DCF was less than what was reported in the literature where the degradation percentages were in the range of 30–90% (Buser et al., 1998; Zhang et al., 2011; Bartels and von Tümpling, 2007).

As mentioned earlier, the number of photolytic degradation products of DCF that have been reported in the literature are in the range of 1 up to 13. It has been reported that three main types of transformation products are formed as a result of DCF photodecomposition: UV-stable products, UV-metastable products, and UV-sensible products (Bartels and von Tümpling, 2007). UV-sensible products could compete with DCF in the photodegradation process. The other products are recalcitrant. Hence, their formation and persistence under sunlight is the reason why the solution changed into clear brownish color at time of exposure (supplementary material Fig. S2). It is worth noting that Keen et al., 2013 (Keen et al., 2013) have reported that these products may in fact be dimers.

These stable products could act as 'inner' filter and deprive sunlight to reach DCF (Agüera et al., 2005). Therefore, the accumulation of

Table 3
Percentage degradation and transfer of pharmaceuticals for solar still and thermal only modes.

		Solar still	40 °C	50 °C	60 °C
AMP	% deg	39 ± 2	1.1 ± 0.2	30 ± 0.8	38 ± 0.6
	% tran	0.00	0.00	0.00	0.00
DCF	% deg	50 ± 3	6.8 ± 0.4	23 ± 0.7	26 ± 0.6
	% tran	0.00	0.00	0.00	0.00
CBZ	% deg	52 ± 5	4.0 ± 0.2	7.6 ± 0.2	58 ± 0.3
	% tran	0.00	0.00	0.00	0.00
NPX	% deg	100 ± 0.00	0.10 ± 0.05	1.2 ± 0.08	88 ± 0.8
	% tran	0.00	0.00	0.00	0.00
IBU	% deg	38 ± 2	1.2 ± 0.6	1.1 ± 0.6	1.1 ± 0.4
	% tran	0.6 ± 0.3	0.8 ± 0.1	2.1 ± 0.3	1.7 ± 0.2

Table 4
Percentage degradation of pharmaceuticals for solar only mode.

CSP 62 ×	% degradation				
	AMP	DCF	CBZ	NPX	IBU
0 s (initial)	0.00	0.00	0.00	0.00	0.00
30 s	0.00	20	0.06	5	1
60 s	0.00	26	0.06	6	1.5
90 s	0.00	29	0.10	7	2
180 s	0.00	44	0.24	13	2
2 h*	0.00	74	0.40	71	6

* Under regular sunlight.

Table 5
Presence, number and retention time of degradation byproducts.

	Byproducts	AMP	DCF	CBZ	NPX	IBU
Solar distillate	Presence	No	Yes	No	Yes	No
	Number, retention time	n/a	1 @ 8.85 min	n/a	2 @ 6.2 and 9.5 min	n/a
Solar residual	Presence	No	Yes	No	Yes	No
	Number, retention time	n/a	1 @ 6.11 min	n/a	2 @ 6.2 and 9.5 min	n/a
Thermal distillate	Presence	No	No	No	No	No
	Number, retention time	n/a	n/a	n/a	n/a	n/a
Thermal residual	Presence	No	No	No	No	No
	Number, retention time	n/a	n/a	n/a	n/a	n/a
CSP	Presence	No	Yes	No	Yes	No
	Number, retention time	n/a	Numerous	n/a	Numerous	n/a

phototransformation products inside the solar still prevented the degradation of DCF from reaching completion.

Six tests (two duplicate tests for each temperature) conducted under thermal only mode showed low degradation of DCF at 40 °C (7%), this increased to reach 23% at 50 °C and slightly increased to 26% at 60 °C. Similarly, as in the solar mode, transfer of DCF was insignificant. However, byproducts were not detected in the residual or in the distillate.

The temperature gradient effect played a role in improving thermal degradation. In the present setup, the solution was heated using a heating mantle, and not an oven. This was necessary to ensure the condensation process on the cover and thus distillation; however, this could have created very slow convection currents. Convection currents may have played a role in increasing the rate of degradation by inducing a slow mixing process not present in stationary systems.

DCF under light only mode showed the highest degradation rate compared to other selected pharmaceutical. It showed 44% and 74% degradation over 180 s of concentrated sunlight and over 2 h of regular sunlight, respectively. This observation confirmed the photosensitivity of DCF. However, in the solar still setup, the photolysis of DCF was impaired by an inner sunlight barrier of accumulated brown transformation products as shown in Fig. S2 of the supplementary material.

3.2.3. Carbamazepine (CBZ)

The absorbance spectrum of CBZ showed an extension to 320 nm (Fig. 5). Despite of its capability of absorbing sunlight UV radiation, its photodegradation is relatively slow (Doll and Frimmel, 2003; Tixier et al., 2003).

In the solar still mode about half of CBZ was degraded (52% SD 5) in the residual of the solar still over a 12 h period of sunlight exposure.

However, the literature indicates that a longer exposure time is required to attain such degradation levels. For example, (Andreozi et al., 2002) (Andreozi et al., 2002) reported that the half-life of CBZ under sunlight was approximately 122 h, whereas a lower half-life of CBZ under sunlight (72 h) was obtained by Matamoros et al. (2009) (Matamoros et al., 2009). Both solar degradation studies showed that CBZ was more persistent when using the glass or quartz reactors compared to solar stills adopted in this study.

The synergetic effect of sunlight and elevated temperatures could explain the reason why the degradation rate of CBZ was higher in the present tests in comparison to those reported in the literature. A study by Yamamoto et al. (2009) showed a relation between photodegradation and external temperature, whereby the results indicated that CBZ was stable in May ($T = 25$ °C) over 70 h of sunlight exposure (Yamamoto et al., 2009). However, about 40% degradation percentage over 50 h of sunlight exposure was recorded in August ($T = 39$ °C). Half-life was reduced intensely from 2100 h in May to 86 h in August. Beside the effect of light intensity, the temperature influence is inevitable and should be taken into consideration.

The transformation products of CBZ were not detected in this study. However, it was repeatedly predicted that 10,11-epoxycarbamazepine is the major product of CBZ photolysis (Lam and Mabury, 2005). Moreover, no transfer of CBZ into the distillate was detected over the whole sunlight exposure period. It is worth noting that contradictory results can be found in the literature. Donner et al., 2013 (Donner et al., 2013) reported photolytic degradation of CBZ with the degradation products proving to be more toxic than the parent compound. More recently Yang et al., 2016 (Yang et al., 2016) confirmed earlier results where it was found that sunlight caused minimal degradation of CBZ.

In a recent review by Mathon et al., 2016 (Mathon et al., 2016), it was reported that the number of photo degradation products for CBZ varied from 1 up to 9, while, Yang et al., 2016 (Yang et al., 2016) reported that sunlight caused minimal degradation of CBZ.

CBZ in the thermal-only mode showed limited degradation of 4% and 8% at temperatures 40 and 50 °C, respectively. However, thermal degradation of CBZ reached 58% at 60 °C. By comparison with the solar still mode where a similar degradation percentage (52%) was achieved, it could be deduced that temperature had a major impact on the degradation process of CBZ.

Insignificant degradation of CBZ was obtained under both concentrated sunlight and regular sunlight with only 0.2% and 0.4% degradation, respectively. This indicates that CBZ is slightly photosensitive, but rather its degradation in the solar still was predominately thermal.

3.2.4. Naproxen (NPX)

The absorption spectrum of NPX (Fig. 5) shows a maximum at 230 nm, and extends into the solar UV spectrum of absorption

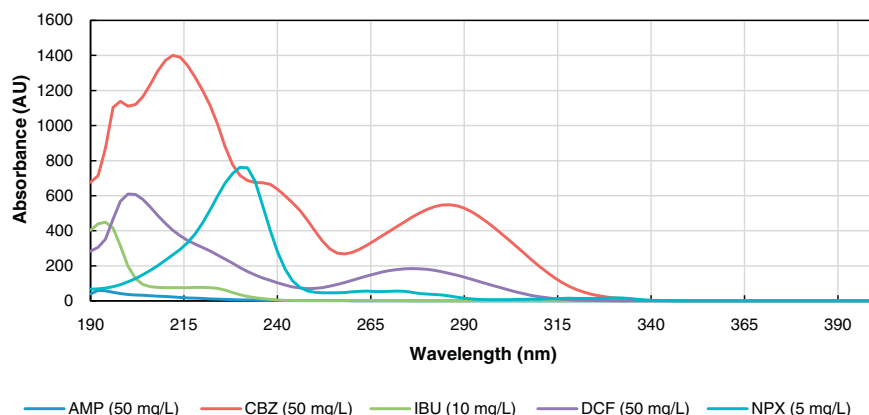


Fig. 5. Absorbance spectra of all pharmaceuticals as prepared and used in the three different modes.

wavelengths greater than 290 nm up to 340 nm indicating its possibility of direct photolysis.

All of the six tests in the solar still mode showed full degradation of NPX in the residual. This is consistent with previous studies (Kanakaraju, 2013; Packer et al., 2003; Felis et al., 2007; Ma et al., 2014; Oppenländer, 2003).

As a result of NPX photolysis, two transformation products were detected in the residual. One of the byproducts showed a retention time of 6.2 min and the other showed a retention time of 9.5 min with respect to the HPLC method described in **Table S1 of the supplementary material**. Both byproducts were also detected in the distillate, indicating higher potential of transfer compared to the parent compound NPX which did not show any transfer at all. In the absence of advanced analytical methods it is postulated that NPX is predominately susceptible to decarboxylation under direct photolysis in aqueous systems (Boscá et al., 2001). The decarboxylated intermediate readily undergoes hydroxylation and oxygenation in the presence of oxygen and two main photoproducts were predicted: ketone adduct and alcoholic adduct, as a result of the formation of a carbonyl group and a hydroxyl group at the position of decarboxylation, respectively (Boscá et al., 2001; Arany et al., 2013; Marotta et al., 2013). Similarly, in this study, it was assumed that these two photoproducts were formed. The photoproduct that appeared at retention time of 9.5 min could be the alcoholic adduct (higher polarity), and the one that appeared at retention time of 6.2 min could be the ketone adduct (lower polarity). However, it should be noted that photolysis of NPX has been reported to result in the formation of five (Jallouli et al., 2016) and six transformation products (Fatta-Kassinos et al., 2011).

As for the thermal only mode, and at temperatures of 40 °C and 50 °C, NPX showed insignificant thermal degradation: 0.1% and 1.2%, respectively. However, the degradation of NPX increased reached to 88% at 60 °C. It could be hypothesized that a fragile bond was cleaved, most probably the carboxyl group bond, when the temperature was maintained high at 60 °C, but this suggestion was not confirmed due to insufficient data relative to the byproducts. Moreover, no transfer was encountered for NPX at all selected temperatures.

NPX showed the second highest degradation rate under light – only mode of about 13% and 71% over 180 s of concentrated sunlight and 2 h of regular sunlight, respectively. Although NPX reached full degradation in the solar still, however, when the light factor contribution was over a short period it showed less degradation. This indicates that NPX degradation could be both light and temperature dependent.

3.2.5. Ibuprofen (IBU)

The absorption spectrum of IBU (Fig. 5) showed a maximum at 194 nm and an insignificant absorbance at wavelengths greater than 240 nm.

Six tests in the solar still mode showed an average of 38% (SD = 2) degradation of IBU in the residual. As pharmaceuticals with chromophores that absorb at wavelengths greater than 290 nm are expected to undergo direct photolysis under sunlight (Kanakaraju, 2013), IBU showed no absorbance beyond 290 nm and it was therefore deemed to be relatively stable. This has been confirmed by a number of studies (Yamamoto et al., 2009; Silva et al., 2014).

However, experimental results indicated instead a fair level of degradation. This observation could be attributed to the synergetic effect of sunlight and temperature.

Other laboratory studies indicated that IBU was susceptible to photodegradation where degradation rates varied from 90% (Epold et al., 2012) to 60% (Giri et al., 2010). More recent studies have confirmed the photolysis of IBU and have reported on the identification of degradation products where (Jakimska et al., 2014) (Jakimska et al., 2014) identified five transformation products whereas Li et al., 2015 (Li et al., 2015) reported the presence of degradation products, without identifying them, and reported that they had higher toxicity levels compared to the parent compound.

To date, and to the authors' best knowledge, the synergetic effects of photolysis and thermal effects on the degradation of pharmaceuticals, and in particular IBU, have not been undertaken. Most studies that used artificial lamps supplied their reactor with a cooling setup to maintain temperature below 25 °C (Epold et al., 2012; Giri et al., 2010; Li et al., 2015). In addition, other studies, which focused on the effect of natural sunlight, studied IBU degradation in surface water under environmental temperature variations (Tixier et al., 2003), or used transparent reactor vessels which maintained a constant room temperature (Yamamoto et al., 2009).

In the present study, the black Teflon plate placed inside the solar still was capable of increasing the temperature to a maximum level between 50 °C and 60 °C (Fig. 2). IBU was the only pharmaceutical that showed transfer by vapor. This is because it has the highest Henry's constant value among the other selected pharmaceuticals. About 0.6% (SD = 0.3) of the initial amount of IBU was transferred to the solar still distillate.

Six tests (two duplicate of each temperature) conducted under the thermal mode in the dark showed very low degradation of IBU, around 1%, at $T = 40, 50$ and 60 °C. This indicates that temperature alone is not sufficient to induce IBU degradation without sunlight. In addition, transfer was also obtained in the thermal mode at all studied temperatures with a maximum of 2% transfer at $T = 50$ °C. The stability of IBU at high temperatures ($T = 20, 40, 60$ and 80 °C) was also reported in a thermodegradation study by (Méndez-Arriaga et al., 2008) (Méndez-Arriaga et al., 2008).

The degradation of IBU under light only mode without temperature interference was very minor confirming that IBU is relatively stable under light. For example, only 2% were degraded over 180 s under concentrated light and 6% over 2 h of exposure to regular sunlight.

This implies that neither the light factor alone nor the temperature factor alone is sufficient for inducing significant decomposition of IBU, but rather the synergetic effect of both factors is crucial for achieving better ibuprofen degradation as in the case of the solar still.

3.3. Environmental relevance, practical implications and limitations

The detection and identification of degradation products “require technologically advanced, costly analytical methods with very high sensitivity” (Fatta-Kassinos et al. (2011); Mathon et al. (2016)). These analytical methods and tools are not currently available and, therefore, the approach adopted has been limited to establishing whether degradation products are present in the distillate and the residual without identifying these by-products or determining their toxicity levels.

Although the concentrations of pharmaceuticals used in the experimental study were much higher than those encountered in the environment (mg/l versus µg/l and in some cases ng/l), the level of transfer of pharmaceuticals and their byproducts to the distillate was extremely low. Given that degradation is often dependent on the initial concentration present, it may be warranted to assume that, at the levels prevalent in the environment, the amount and concentration of pharmaceuticals and their byproducts that may transfer to the distillate in solar stills may not constitute an environmental risk/hazard and that the water produced may be fit for human consumption. However, the residue/brine containing the degraded and parent pharmaceuticals will constitute an environmental risk if discharged without treatment. It is anticipated that an advanced indirect photolytic process combined with an advanced oxidation process will mineralize the pharmaceuticals and their degradation byproducts and render the brine suitable for discharge.

It is also worth noting that the experiments were conducted under “controlled” conditions to determine the combined effects of thermal and direct photolysis. For commercial solar stills, the raw water used will contain suspended solids, turbidity, natural organic matter, a variety of mineral salts, constituents that will, inevitably lead to indirect photolysis, which when combined with the natural photolysis and thermal

effects may result in higher degradation percentages and possibly mineralization.

4. Conclusions

This study has demonstrated that transfer and degradation of pharmaceuticals in solar stills are dependent on the pharmaceutical type, Henry's constant, thermal stability and, in a number of instances, on the synergistic effects of direct photolysis and thermal effects. The transfer percentage of the parent compound remains very low compared to initial concentration with the maximum value obtained being 2% in the case of IBU which was the only pharmaceutical that showed transfer in its initial form. NPX and DCF did not transfer in their initial form, however after exposure to direct sunlight, their byproducts of degradation were transferred to the distillate. In the case of NPX, high intensity solar radiation resulted in an array of up to 10 different unidentified byproducts, where some of these may be more toxic than their parent compound.

In addition, the study also showed that in the case of AMP, NPX and CBZ, degradation is characterized by a temperature threshold beyond which a high rate degradation of the compounds is induced. NPX, IBU and CBZ required both high temperature and sunlight combined to degrade effectively. Concentrated solar power accelerated the degradation of DCF, NPX and IBU with a three-minutes-degradation percentage of 44%, 13% and 2% respectively.

The results of the experimental work have shown that in solar stills, a combination of thermal degradation and direct photolysis may lead to the partial degradation of otherwise recalcitrant pharmaceuticals and to the transfer of volatile degradation products to the distillate which, at the large concentrations considered in this work may render it potentially unsafe. However, it has also been demonstrated that for certain types of pharmaceuticals the distillate did not contain any traces of the parent pharmaceutical or its degradation byproducts.

Conflict of interest

This research was funded by a research grant from the Lebanese National Council for Scientific Research (NCSR) (NCSR-01-12-12). NCSR didn't intervene in any of the actions bellow:

Study design

Collection, analysis and interpretation of data

Writing of the report

The decision to submit the article for publication

There is no conflict of interest of any form or type.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.09.082>.

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