The Synthetic Opioid Fentanyl Is Degraded By Temperature And Ultraviolet Irradiation In The Environment

Raven Reitstetter and Travis Losser*
Chemical Test Division, West Desert Test Center, Dugway Proving Ground, Dugway, UT 84022
**Corresponding Author – raven.e.reitstetter.civ@mail.mil*

Abstract

The ever increasing use of pharmaceuticals to improve quality and length of life results in an increasing release into the environment through waste water treatment facilities, improper disposal of unused drugs and illicit drug manufacture and use. In this way pharmaceutical compounds end up in sewage sludge, water and soil. The stability and breakdown processes of synthetic opioids in the environment are not completely understood. Here, we show that synthetic opioids, exposed at the surface, are broken down by irradiation and temperature. Pharmaceuticals entering the environment are usually sequestered into soil, sewage sludge or water. A fraction of these compounds is also exposed at surfaces. We applied the synthetic opioid fentanyl on filter paper and mixed with soil as a model for synthetic opioids released to the environment. Preliminary results show that ultraviolet irradiation at a wavelength and radiant flux similar to sun exposure degraded fentanyl over a period of four days. In a similar fashion temperature broke down fentanyl, although to a lesser extent. Thus, surface-exposed synthetic opioids are degraded by sun exposure and temperature. These results may also indicate that synthetic opioids segregated into at least the upper soil layer may be degraded by temperature alone.

Introduction

An increasing population coupled with an increase in the elderly and improvements in health care has led to rising use of pharmaceuticals. Increased use of pharmaceuticals, however, is not limited to the human population. Livestock use of pharmaceuticals has also shown increases. The rise in use of pharmaceutical agents is coupled with their release into the environment through waste-water treatment plants and landfills or direct discharge. The increasing use of illicit drugs is another area of concern for unregulated disposal of unused drugs via toilets, sinks, garbage or direct disposal into the environment. This situation is further complicated by the existence of clandestine drug labs that produce illicit drugs in an uncontrolled environment.
Fentanyl and a variety of fentanyl derivatives have surfaced as an emerging illicit drug problem through drug use and manufacture with the potential of environmental release and pollution. Since we have very little information on the environmental fate of fentanyl we embarked on an investigation to look at the persistence and degradation of fentanyl in soil. Here we report on our initial findings of fentanyl degradation on glass fiber filters, as a surrogate for fentanyl deposition on a surface. Our results show that fentanyl is degraded by light exposure.

Materials and Methods

Irradiation of samples was conducted at constant exposure 254 nm emanating from a UV light mounted in a dark chamber for up to four days. Glass fiber filters were spiked with 10 µg (dissolved in 100 µl methanol) fentanyl citrate each. Triplicate samples were removed from the irradiation box and extracted with acetonitrile containing 1% formic acid on days 1, 2, 3, and 4. Extracted samples were analyzed by LC-MS. An extraction control and a non-irradiated control were included in the study. The radiant flux within the chamber was measured with an irradiance meter. The temperature in the chamber was monitored with a digital thermometer. The absorbance of fentanyl in a methanol solution was determined with UV-VIS spectroscopy in the spectral range of 200-800 nm. Outdoor irradiation was measured with the UVC light meter in June 2017 in the morning and afternoon. On both occasions six 10 minute measurements were taken each and averaged for a 60 min time frame.

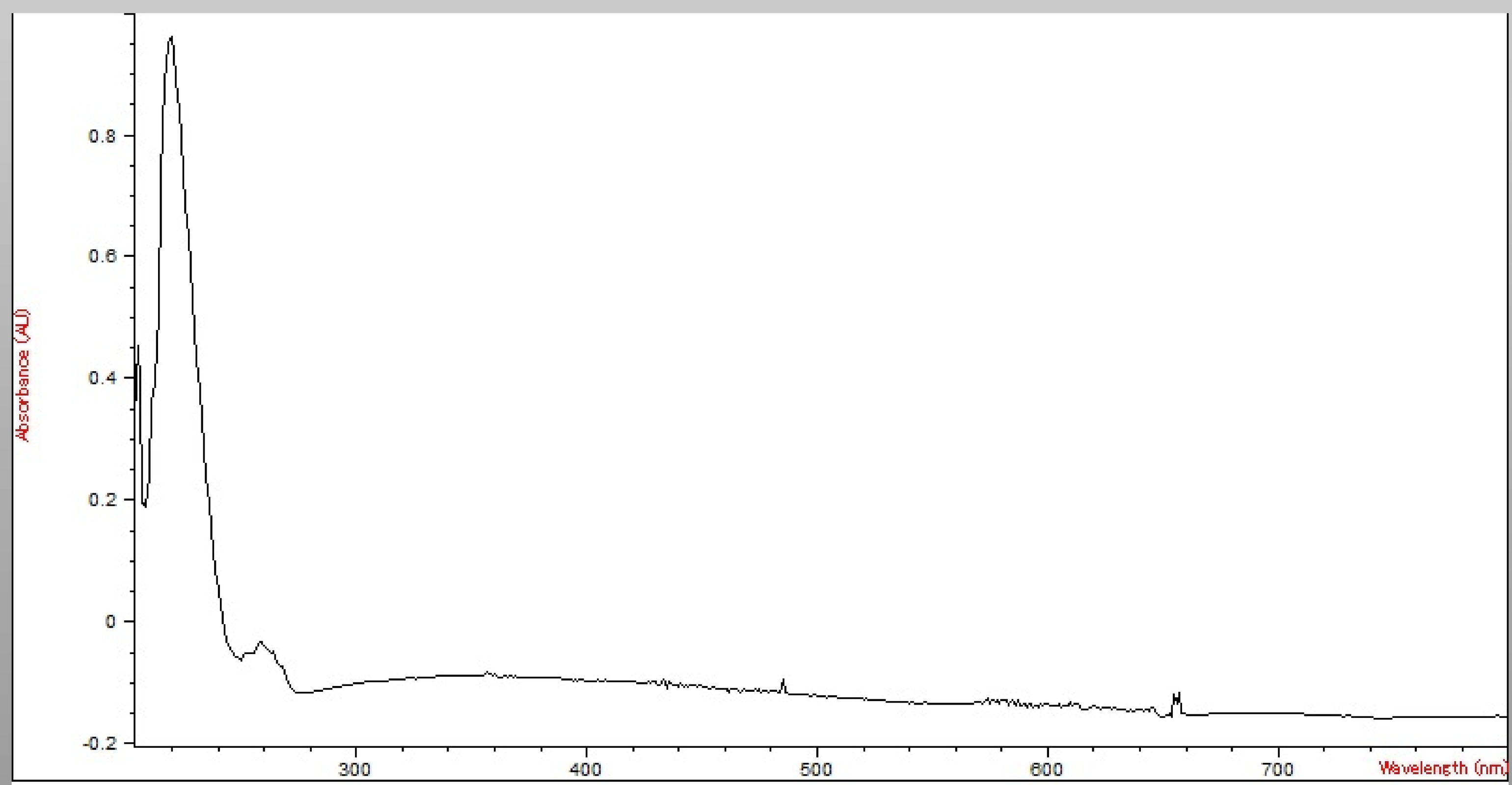

Figure 1. UV-VIS spectrum of 0.1 mg fentanyl citrate in methanol between 200 and 800 nm. Three absorbance peaks are visible at 205 nm, 220 nm and 258 nm, respectively.

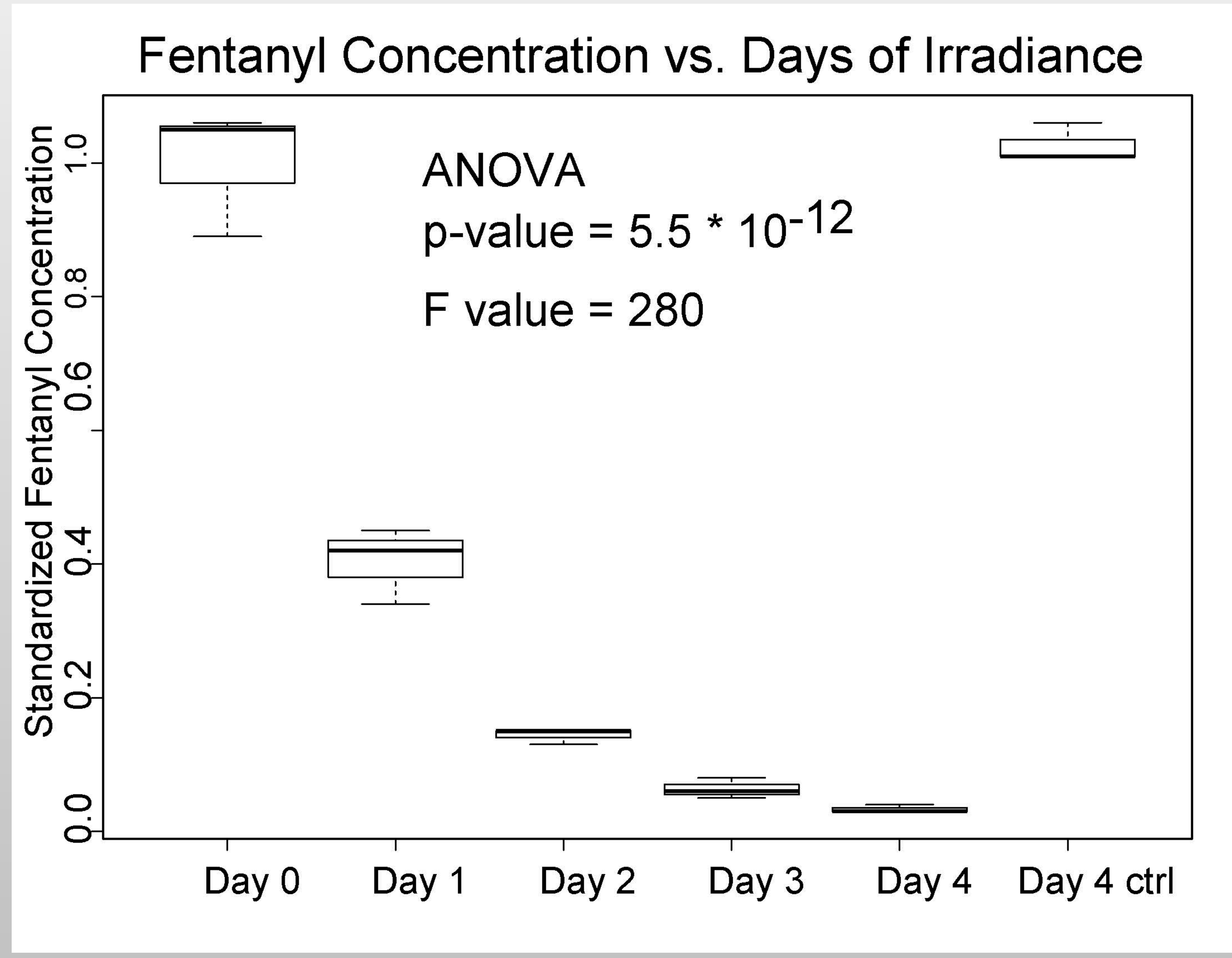

Figure 2. Amount of fentanyl on filter paper is reduced by irradiation at 254 nm and a temperature of 40 ºC over the course of 4 days. Dark controls held at 25 ºC did not show a reduction in the amount of fentanyl after 4 days. The fentanyl concentration between individual days was tested by ANOVA.

Irradiance Regimen			
	laboratory conditions		
	Cumulative Irradiance [µW/cm^2]	cumulative time [h]	"10 h outdoor days" equivalent
Day 1	679.5	4.5	0.6
Day 2	4228	28	3.8
Day 3	7852	52	7.0
Day 4	11400.5	75.5	10.2

Table 1 : Irradiance regimen for fentanyl-spiked filters and equivalent exposure days in a 10 hour daylight equivalent.

Results and Discussion

Three absorbance peaks for 0.1 mg/ml fentanyl in methanol were visible at 205 nm, 220 nm and 258 nm measured with a UV-VIS spectrophotometer indicating that fentanyl strongly absorbs in the UV part of the sunlight spectrum (Fig1).
Fentanyl irradiated on filters for 1 to 4 days with 254 nm UV light exhibited an exponential decay (Fig. 2). The extraction efficiency for extracting fentanyl from filters was 83%. At day four 3% of the original concentration was left on the filters. During the first day of irradiation the temperature within the exposure chamber increased to 42 ˚C and stayed constant at that temperature throughout the study. A subsequent exposure of filters spiked with fentanyl and incubated at 42 ˚C (without irradiation) showed degradation by temperature alone at day 4 with 28% fentanyl remaining on filters. Controls stored at room temperature in the dark did not show any degradation of fentanyl applied to the glass filters.
The strong absorbance peak at 258 is close to the irradiation wavelength of 254 nm. Therefore, it is plausible that absorbance at this wavelength contributed to the photolytic degradation of fentanyl during irradiation with UV light.
The average outdoor irradiance in June for an average 10 h sunlight day was computed by assuming 5 h of low intensity (morning measurement) and 5 h of high intensity (afternoon measurement) sunlight. The day average was then used to compute 10 h outdoor day equivalents corresponding to the cumulative irradiance in the laboratory study (Table 1).

Conclusion and Path Forward

- Surface deposited fentanyl is degraded by UV irradiation and temperature
- The effective wavelength range is present in natural sunlight
- The synergism between irradiation and temperature for fentanyl breakdown will be explored in future experiments
- The efficacy of irradiation and temperature in the breakdown of fentanyl mixed with soil will be determined in future studies

Acknowledgements

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