Landfill Waste Fire Effects Over Town Areas Under Rainwaters

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Abstract. Identifying a dark brown color of the rainwater deposited on the streets after a landfill waste fire, the color persisting few months after the fire, an analysis of water samples collected from the streets after rainfall revealed characteristic compounds as for those resulted from urban waste combustion. A simulation of burning waste materials specific to be thrown on the landfill was conducted in the laboratory and the resulting ashes have been analyzed and compared with the dry material obtained from the rain waters collected. FTIR spectra of the two samples proved noticeable similarity among them, evidencing very toxic components, both organic and inorganic, among which dioxins and furans, sulfonic compounds, imines, imides, aromatic and aliphatic nitro and nitroso compounds, HCN and HNO3. Significant fluorescence intensity was determined for the rainwaters using LIF method and peaks specific to dioxin fluorophores were obtained in the resulted spectrum. Therefore, persistent pollution generated by garbage dumps fires is proven herein to affect both air and soil with the possibility to also contaminate town water supply, raising a major threat for human’s health, as well as for vegetation and all livings.

1. Introduction
Identifying a dark brown color of the rainwater deposited after a landfill waste fire, the color persisting few months after the fire, an analysis of water samples collected from the streets after rainfall revealed characteristic compounds as for those resulted from urban waste combustion. It has been proved a long time source of soil level contaminants, but not limited to that, as it has been proved before pollution circuit air – rain – soil – water – back to the air [1, 2]. Previous studies and reports warned of the danger of inducing major pollution by the burning of waste, especially landfill waste, which is a mixture of materials and substances that lead to the formation of high toxicity chemical compounds by combustion, among which, dioxin and furans being by far one of the most dangerous due to their carcinogenic effect [3-7]. Scientists have been concerned to finding methods to reduce and neutralize such emissions [8, 9]. Emissions of other very dangerous chemical species due to their toxic effects, such as cyanates and cyanides, including HCN, have been reported in forest or vegetation wildfires. Taking in consideration that landfill waste is a mixture of materials and substances that reflect the waste incineration mills, only being open fires, but also being associated to hazardous fires of vegetation, the magnitude of the damages to environment due to pollutants is highly enhanced. The study presented herein is aimed to evaluate long time damages of landfill waste fire, its persistence and extensive spread under rainwater effects in atmosphere and on soil. A landfill waste fire in Romania, which had lasted for two weeks before being extinguished, proved to be a long time source
of soil level contaminants. Dark brown color of the rain waters on the streets persisted after few months from the fire episode and its strong smell obviously denoted extremely high contamination.

2. Methods and materials
Samples of rainwaters were collected from the streets after few months from the landfill waste fire and analyzed. The sample of water was dried on a glass slab and the resulted solid phase was grated out and then analyzed with FTIR spectroscopy to identify chemical groups and chemical species assessed to those. In order to receive as much accurate information, the landfill waste fire was simulated in laboratory, burning different materials together. The resulted ashes and incompletely combusted materials were washed with water and the resulted residual waters were processed for FTIR analysis after that using the same as proceeded with the rain waters collected from the streets. Three combinations of materials were used in the simulations:

S1: polystyrene, wool, cardboard, wrapping foil for aliments, cotton, plastic, paper, wood;
S2: wool, cardboard, wrapping foil for aliments, cotton, plastic, paper, wood, polyacrylonitrile, leaves, pectin, detergent, earth, which means (S1 – polystyrene) + (polyacrylonitrile, leaves, pectin, detergent, earth);
S3: wool, cardboard, wrapping foil for aliments, cotton, plastic, paper, wood, polyacrylonitrile, leaves, pectin, detergent, earth, aluminum foil, which means S2 + aluminum foil. Furthermore, the water collected from the street of Horezu (Horezu sample) was analyzed with laser induced fluorescence (LIF) as well as UV-Vis absorption.

3. Results and discussions
3.1. Fourier transform infrared spectroscopy (FTIR)
The source of pollution detected on the streets of Horezu is proven the landfill waste fire by the good similitude between the FTIR spectrum of the rainwaters collected from the streets of Horezu (Horezu sample) and the two simulation samples S2 and S3, as seen in Figure 1 (b).

![Figure 1. FTIR spectrum of: (a) waters collected from the streets of Horezu after rain (Horezu); (b) FTIR compared spectra of waters collected from the streets of Horezu after rain (Horezu) and residual waters after washing the burnt mixtures as described before (S1, S2, S3).](image-url)
Based on the FTIR spectra of the Horezu sample (Figure 1a), also compared to the S1 and S2 simulation samples (Figure 1b), aliphatic and aromatic structures were identified, as well as the functional groups attached to them. Thus, the composition of the pollutants from the Horezu sample could be evaluated, as well as the sources, respectively the waste materials from the landfill waste that generated them because of the combustion. The results are centralized in Table 1.

Table 1. FTIR spectrum bands interpretation.

| Component                   | Spectrum bands (Figure 1) and associated groups [10, 11] | Sources in the waste combustion |
|-----------------------------|----------------------------------------------------------|----------------------------------|
| **aliphatic groups**        | **2930 cm⁻¹, 2855 cm⁻¹ C-H aliphatic stretching vibrations** | Cardboard, paper, food wastes, as well as combustion of other materials with aromatic, phenolic structures |
| **-CH₂ - CH₂ - aromatic**   | Aromatic C-H stretching in the range 3080 – 3030 cm⁻¹ overlapping with the wide band at 3442 cm⁻¹; 1580 cm⁻¹ aromatic C – C stretching, ring skeleton vibration; 1202 cm⁻¹ aromatic C – H in plan deformation; 680 cm⁻¹ C – H out of plan deformation | |
| **heteroaromatic groups**   | (aromatic) **dioxin** (2,3,7,8-tetrachlorodibenzo-p-dioxin) | |
|                             | (heteroaromatic) **furans** (oxacyclopentadiene) | |
| **1055 cm⁻¹ and 879 cm⁻¹: C – O – C symmetric and asymmetric stretching; 834 cm⁻¹ C-Cl stretching; 745 cm⁻¹ heteroaromatic C – H out of plan deformation** | Plastic, dyestuffs, detergents combustion | |
| **(heteroaromatic) **pyrrole** | 3442 cm⁻¹ NH stretching vibration free and H-bonded; 745 cm⁻¹ C – H out of plan deformation | |
| **(heteroaromatic) **pyridine** | 1640 cm⁻¹ C = N stretching vibration; | Polyacrylonitrile |
| **(aliphatic and aromatic) **imine** | 1640 cm⁻¹ C = N stretching vibration; 3442 cm⁻¹; 3738 cm⁻¹; 3850 cm⁻¹ O – H stretching vibrations | Leaves combustion |
| **and oxime** (aldoxime -1 and ketoxime - 2) | | |
Component Spectrum bands (Figure 1) and associated groups [10, 11] Sources in the waste combustion

| Source | Spectrum Bands and Functional Groups |
|--------|-------------------------------------|
| Sulfoxides | 1055 cm\(^{-1}\) S = O stretching; 1403 cm\(^{-1}\) - SO\(_2\) stretching asymmetric; in the same range R – SO\(_2\) – hal 1202 cm\(^{-1}\) - SO\(_2\) stretching symmetric; in the same range R – SO\(_2\) – hal 879 cm\(^{-1}\) S – O stretching; | Detergents, bleachers combustion |
| Thiols and sulfides | 2582 cm\(^{-1}\) – 2382 cm\(^{-1}\) S – H stretching vibration 879 cm\(^{-1}\) S – H deformation vibration; 745 cm\(^{-1}\) C – S stretching vibration | Wool combustion |
| Cyanates, cyanides and dyazo-components | 2300 – 1996 cm\(^{-1}\) OC \(\equiv\) N; C \(\equiv\) N; \(-N^+\) \(\equiv\) N stretching; | Polyacrylonitrile, organic dyes |
| Epoxides and peroxydes | 3442 cm\(^{-1}\) O – O – H stretching; 1202 cm\(^{-1}\) C – O – O stretching; 834 cm\(^{-1}\) O – O stretching. | Bleachers, paper |
| Formates and benzoates | 1580 cm\(^{-1}\) (COO\(^{-}\)) stretching asymmetric; 1403 cm\(^{-1}\) (COO\(^{-}\)) stretching symmetric; 745 cm\(^{-1}\) (COO\(^{-}\)) deformation vibration in formates; 680 cm\(^{-1}\) (COO\(^{-}\)) deformation vibration in benzoates | Textiles (wool, PAN, cotton), processed wood, plastics, detergents |

Based on Table 1, vibrational bands of aliphatic, aromatic and heteroaromatic groups are evidenced, as well as other specific groups added to the first ones, according to which the substances that resulted from combustion are identified. Thus, the aliphatic groups are denoted by the bands at 2930 cm\(^{-1}\), 2855 cm\(^{-1}\) for C-H stretching vibrations. Bands in the aromatic range C-H stretching vibrations may be overlapping with the 3442 cm\(^{-1}\) very broad band. Aromatic C-C stretching vibration in 1590 cm\(^{-1}\) – 1560 cm\(^{-1}\) range and aromatic C-H in plan deformation in the range 1250 cm\(^{-1}\) – 950 cm\(^{-1}\) and C – H out of plan deformation in the range 900 cm\(^{-1}\) – 650 cm\(^{-1}\) confirm the aromatic structures. Ring skeleton in the 1590 cm\(^{-1}\) - 1560 cm\(^{-1}\) range is also specific to heteroaromatic compounds (dioxin, furans, pyridines, pyrrole, and others) denoted by the bands in the range 990 cm\(^{-1}\) – 725 cm\(^{-1}\) of the C – H out of plan deformation in heteroaromatic groups. In addition to the ring skeleton vibration, the heteroaromatic species are also evidenced by specific functional groups vibrations, namely pyrrole structure is evidenced by the 3442 cm\(^{-1}\) band of NH stretching vibration,
Thiols are also evidences of carboxylates with the d for each simulation and provides information on the presence. Imine en 30 ns delay and d sample compared with the Horezu sample and S1, S2 spectra shows the cis emission for both 30 ns delay and 50 ns delay, the emission after 50 ns presenting shifts to lower wavelengths (hypsochromic shift or blue shift). Bands within 406 nm – 593 nm could also indicate benzofurans of different structures as per Jérémie Grolleau et al [21] fluorescence analysis, despite slight shifts, but as measurements conditions are different, we cannot precisely tell if they are exactly the same structures in the study presented herein. Moreover, the bands shifts between 30 ns delay and 50 ns delay for the same sample show how important the conditions and parameters of the method used for fluorescence analysis are. The shift in the LIF spectra of Figure 2 could denote either tautomeric structures changing during emission, or free radicals formation and other reactions in process, as well as Swan peaks organic carbon generated during laser interaction with the organic compounds in the sample of water [22-25].

pyridine by 1640 cm\(^{-1}\) band of C = N stretching vibration; and dioxin by C – Cl stretching vibration at 834 cm\(^{-1}\). Other chemical species denoted by their specific groups are imine and oximes with C = N stretching vibrations at 1640 cm\(^{-1}\), oxime being also denoted by the 3442 cm\(^{-1}\), 3850 cm\(^{-1}\) and 3738 cm\(^{-1}\) bands of O – H group stretching. Bands at 1055 cm\(^{-1}\), 1403 cm\(^{-1}\), 1202 cm\(^{-1}\), 879 cm\(^{-1}\) are evidence of sulfoxides and sulfones. Thiols and sulfides specific bands are indicated by the bands in the range 2582 cm\(^{-1}\) – 2382 cm\(^{-1}\) and 745 cm\(^{-1}\), while cyanates and cyanides are indicated in the range 2300 cm\(^{-1}\) – 1996 cm\(^{-1}\) of weak bands. Testing with gas sensor the emissions of rainwaters collected from the streets of Horezu (Horezu sample), HCN was detected. The bands of 3442 cm\(^{-1}\), 1202 cm\(^{-1}\) and 834 cm\(^{-1}\) may also indicate epoxides and peroxides. There are also evidences of carboxylates with the 1580 cm\(^{-1}\), 1403 cm\(^{-1}\) bands, as formates (745 cm\(^{-1}\)) and benzoates (680 cm\(^{-1}\)) [10, 12, 13]. As the band at 1640 cm\(^{-1}\) is in the same range with C=O, formaldehyde and urea formaldehyde could be also in the mixture of chemicals resulted from waste combustion [1]. The difference in the FTIR spectrum of S1 simulated sample compared with the Horezu sample and S1, S2 spectra shows the influence of the added “waste materials”. The missing band at 1640 cm\(^{-1}\) of C = N vibration in the spectrum of S1 sample shows that imine, oxime and pyridine didn’t result from its combustion. Imine and oxime result from leaves combustion and the source of pyridine in S2 and S3 simulation samples is polyacrilonitrile combustion. Both, leaves and polyacrilonitrile, missing from the S1 initial mixture, the result reflects the composition used for each simulation and provides information on the presence of imines, oximes and pyridine in the composition of Horezu sample. In the rainwaters collected from the streets of Horezu (Horezu sample), toxic substances on which the World Health Organization warns were thus detected by the FTIR method. Among all, dioxin and dioxin-like substances are known for its effects on human’s immunity system, also producing skin lesions, carcinogenicity and other effects on human health. Hydrogen cyanide and cyanides, are also of high toxicity (oral, respiratory and dermal), as well as pyridines, pyrroles, imines and oximes, sulfoxides, sulfones, thiols, sulfides, cyanates, cyanides, dyazo- components, epoxides and peroxides, formates, benzoates.

3.2. Laser induced fluorescence (LIF)
Laser induced fluorescence using pulsed laser beam of 355 nm wavelength and 10 ns pulse width, at 100mJ energy proved high intensity fluorescence for the rainwaters collected from the streets of Horezu (Horezu sample) after few months from the landfill waste fire with time life of 50 ns. The decay of intensity emission was 10 times within 20 ns, noticed between 30 ns delay and 50 ns delay measurements.

Fluorescence spectrum evidences content of aluminum in the waste material that entered into reaction during combustion. The emission at 487 nm from the spectrum of Figure 2 (a) denotes the fluorophore Al (III) that entered in bonds with organic compounds [14], but also a number of chemical compounds of biological origin, including chlorophyll, but also wood lignin, as well as organic pigments and dyes of biological and/or synthetic origin [15-20]. Secondary peaks are noticed in the emission for both 30 ns delay and 50 ns delay, the emission after 50 ns presenting shifts to lower wavelengths (hypsochromic shift or blue shift). Bands within 406 nm – 593 nm could also indicate benzofurans of different structures as per Jérémie Grolleau et al [21] fluorescence analysis, despite slight shifts, but as measurements conditions are different, we cannot precisely tell if they are exactly the same structures in the study presented herein. Moreover, the bands shifts between 30 ns delay and 50 ns delay for the same sample show how important the conditions and parameters of the method used for fluorescence analysis are. The shift in the LIF spectra of Figure 2 could denote either tautomeric structures changing during emission, or free radicals formation and other reactions in process, as well as Swan peaks organic carbon generated during laser interaction with the organic compounds in the sample of water [22-25].
Figure 2. Compared fluorescence spectra 30 ns and 50 ns delay of rain waters collected from the streets of Horezu few months after the landfill waste fire (a), compared fluorescence spectra 30 ns delay of rain waters collected from the streets of Horezu few months after the landfill waste fire and curcumin.

3.3. UV-VIS
Absorbance UV-Vis spectrum of the Horezu sample rainwater (Figure 3) denotes dichloromethane with the peak at 233 nm.

Figure 3. Absorbance UV-VIS spectrum.

3.4. Effects on human health
In the rainwaters collected from the streets of Horezu (Horezu sample), toxic substances on which the World Health Organization warns were thus detected by the FTIR method. Among all, dioxin and
dioxin-like substances are known for its effects on human’s immunity system, also producing skin lesions, carcinogenicity and other effects on human health. Hydrogen cyanide and cyanides, are also of high toxicity (oral, respiratory and dermal), as well as pyridines, pyrroles, imines and oximes, sulfoxides, sulfones, thiols, sulfides, cyanates, cyanides, dyazo- components, epoxides and peroxides, formates, benzoates. UV-Vis spectra of the Horezu sample evidenced dichloromethane, a volatile liquid, producing respiratory disorders, known for inducing germ cell mutagenity and carcinogenicity. Adding the flammable properties of some of the identified substances in the Horezu sample, we have the image of the magnitude of the danger when exposing the population of Horezu to the long-term effects caused by the landfill waste fire.

The morphology meaning the shape of volcanic ashes is depended upon a plethora of diverse eruptions and kinematic processes [46, 47].

Eruptions of less viscous basaltic magmas form droplet-like particles of volcanic ashes which are partly controlled through surface tension, the friction of air, an acceleration of the droplets after leaving the vent of a volcano. The shapes are found ranging from a perfect sphere to variously twisted, elongated droplets having even fluidal surfaces [47].

While the morphology of volcanic ashes from eruptions of highly viscous magmas dependent mostly upon the shape of vesicles in the upcoming magma prior to disintegration. The vesicles are produced through the spreading out of gases embodied with magma prior to solidification of the magma. The particles of volcanic ashes can have dissimilar vesicular particles and vesicularity and also enormously high ratios of surface area to volume [46].

The broken vesicle walls are formed owing to concavities, tubes, and troughs observed on surfaces of grain [47]. Angular, vesicular fragments that are pumiceous or thin vesicle-wall fragments are found occurring in vitric volcanic ashes generated from the eruptions of highly viscous magma. Whereas, the lithic fragments of volcanic ash are found angular to sub rounded in shape. Lithic morphology in volcanic ashes is commonly depended upon the mechanical properties of the wall rock which are shattered by the explosive expansion of gases embodied in magma or spalling when it touches the surface.

The morphology of volcanic ash particles generated through phreatomagmatic types of eruptions is managed by forces present in the chilled magma that result in divisions of the glass to yield small pyramidal or blocky particles of glass ash [48].

In the case of phreatomagmatic types of eruptions, merely a trivial role in the determination of grain shape is played by the density and vesicle shape. In this case, the coming up magma is cooled swiftly when coming into contact with surface or groundwater. The principal kinds of pyroclastic shapes of fragments formed due to the forces in the "quenched" magma are (1) vesicular and irregular but having even surfaces; (2) equant and blocky (3) drop-like or sphere-shaped (3) convoluted and moss-like and, (5) plate-like.

4. Conclusion and perspectives
The mixture of materials of high variety of chemical structures led by combustion to a number of chemical species with significant danger potential to the human health, among which dioxins and furans, pyridines, pyrroles, imines and oximes, sulfoxides, sulfones, thiols, sulfides, cyanates, cyanides, dyazo- components, epoxides and peroxides, formates, benzoates. Since the tests were performed few months after the fire episode on the landfill waste of Horezu, it is proven with the analysis results presented herein the persisting toxicity in the atmosphere and on the soil, “recycled” by rain and evaporation phenomena.

5. References
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