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Un-intentional Persistent Organic Pollutants (UIPOP) Within the Integrated Agricultural Unit of the Sucrivoire Company in Zuénoula

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Abstract: Agro-industrial activities generate discharges likely to harm the environment and public health. This study aims to evaluate the presence of persistent organic pollutants (POPs) in discharges with a view to proposing solutions improving the quality of industrial discharges. The collection data made it possible to identify the sources of production of POPs from the integrated agricultural unit of the Sucrivoire company in Zuénoula as a first step. Secondly, the POPs present in the environment were characterized using the 2013 Toolkit. The results showed that emissions of these pollutants are mainly due to waste incineration activities, transportation and burning of cane plantations before harvest. Dioxins and furans are the most emitted POPs and mainly affect air quality with 27,6 g. Their impact on water and soil remains low or negligible. In view of these results, it was recommended to reduce these emissions and take these pollutants into account in the control of air pollution. The application of these measures requires rigorous monitoring to ensure their effectiveness and achieve the reduction objectives. Strict and sustainable management of waste will help preserve the environment and protect public health.

1. Introduction

Agro-industrial activities represent a very significant source of pollution and contribute to the deterioration of the environment and public health around the world (Djebli and Saifi, 2020). After the second World War, scientists began to recognize that some chemical pollutants were capable of persisting in the environment, migrating through air, water, soil, and sediment, and accumulating to potentially harmful levels for wildlife and human health (El-Shahawi *et al*., 2010). These chemical pollutants are called persistent organic pollutants (POPs). The main goal of any country is to have a healthy environment in order to meet multiple needs (Borote, 2021), (Alaqarbeh *et al*., 2022). In recent decades, POPs have become a major source of interest in human and environmental health. At the Stockholm Convention, held in 2001, these pollutants were recognized as toxic substances and very resistant to degradation by biological, photolytic or chemical processes. They accumulate in ecosystems (Valle *et al*., 2004), (Valle *et al*., 2005) and are spread by air, water and migratory species, far from their sources of production (Travel *et al*., 2012). To date, the incineration of municipal and industrial waste plays a dominant role in the release of dioxins and furans into the environment (Schuhmacher and Domingo, 2006), (Kim *et al*., 2008), (Vilavert *et al*., 2010), (Chiu *et al*., 2011). It is for this reason that the European Committee for Standardization has set a limit of 0.1 ng/m3 for emissions of dioxins and furans from incineration plants. In Côte d'Ivoire, the sugar industry sites, notably that of the Sucrivoire company in Zuénoula, are considered installations classified for environmental protection (ICEP) (Kouamé *et al*., 2010). However, they are likely to generate pollution at several levels through their discharges. Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo-furans (PCDD/PCDF) are persistent organic pollutants formed accidentally during waste incineration and other thermal industrial processes. Once released, they are deposited around the source and accumulate in environments rich in organic matter, mainly sediments and soil.

Soil is the main site of deposition and long-term accumulation of PCDD/PCDF emitted by various sources, unlike air, which is directly exposed to emissions from incineration, but only in the short term. Thus, soil has often been selected by several studies as a model medium for monitoring dioxins and furans in order to estimate the impacts of incinerators (Kim *et al*., 2008), (Abbott *et al*., 1997) and (Caserini *et al*., 2004). It is clear that persistent organic pollutants are not taken into account during the various pollution analyzes in industrial discharges, even though they have effects on the environment and human health (Akartasse *et al*., 2022), (Jones, 2021). The acuteness of the problems linked to unintentional persistent organic pollutants justifies our work on their estimation.

The general objective of this study was to identify the different source activities of production and to characterize the unintentional persistent organic pollutants in the discharges with a view to proposing solutions improving the quality of industrial discharges within the integrated agricultural unit of the Sucrivoire company in Zuénoula.

2. Methodology

2.1 Study area

The Integrated Agricultural Unit (IAU) of the Sucrivoire company is located 25 kilometers northwest of the town of Zuénoula between latitudes 7°37' and 7°39' North and longitudes 6°11' and 6°14 ' West. This city is located approximately 400 kilometers from Abidjan (economic capital) in the Zuénoula department in the Marahoué region, in the center-west of Côte d'Ivoire (Péné and Assa, 2003) (**Figure 1**). Remember that the Sucrivoire company specializes in the exploitation of sugar cane plantations, the production and marketing of sugar.

2.2 Identification of activities that are sources of persistent organic pollutants

It was carried out through guided field visits to identify activities and installations likely to generate persistent organic pollutants with photographic images taken. Also, at each visit, a survey was carried out on site among staff using a questionnaire in order to collect the data necessary for the estimation of these pollutants.

2.3 Characterization of *the agricultural unit unintentional POPs in environmental matrices*

The characterization of the different POPs was done through an estimation using an Excel spreadsheet called Toolkit 2013. It is designed to gather the necessary activity data, provide a means of classifying processes and activities into categories for which appropriate emission factors are provided. The estimate can be calculated from this basic equation: Source intensity (dioxin emissions per year) = "Emissions factor" × "Activity rate".

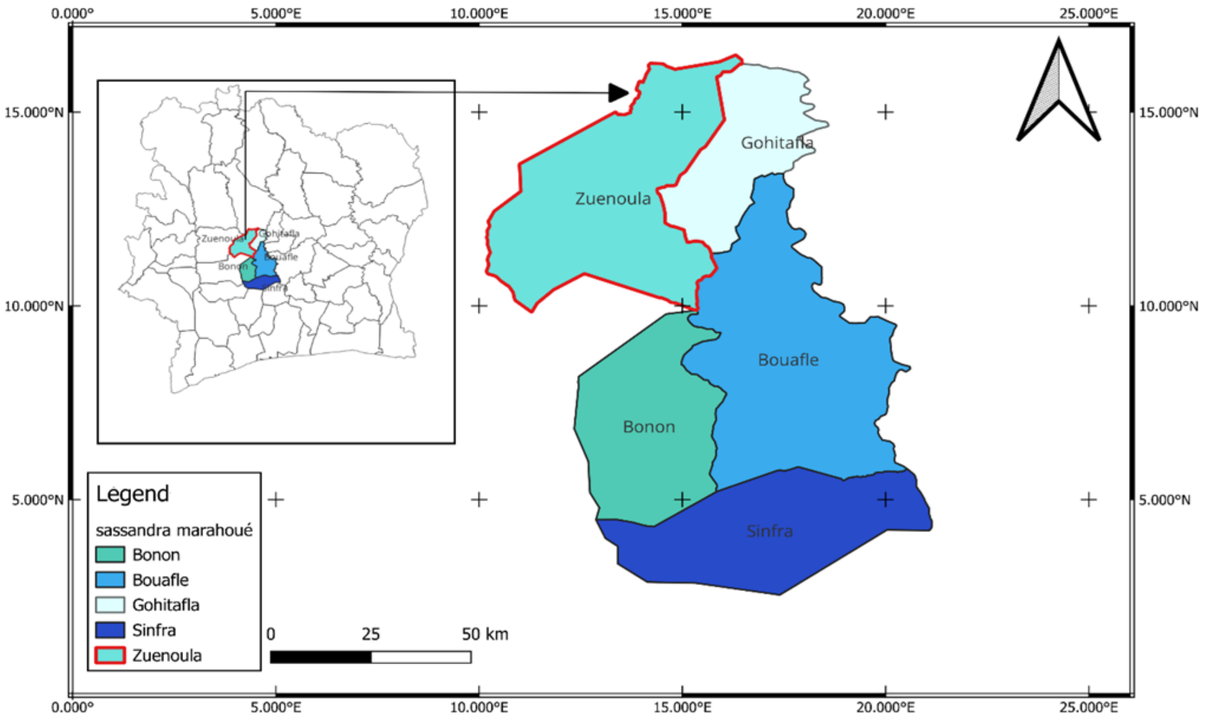
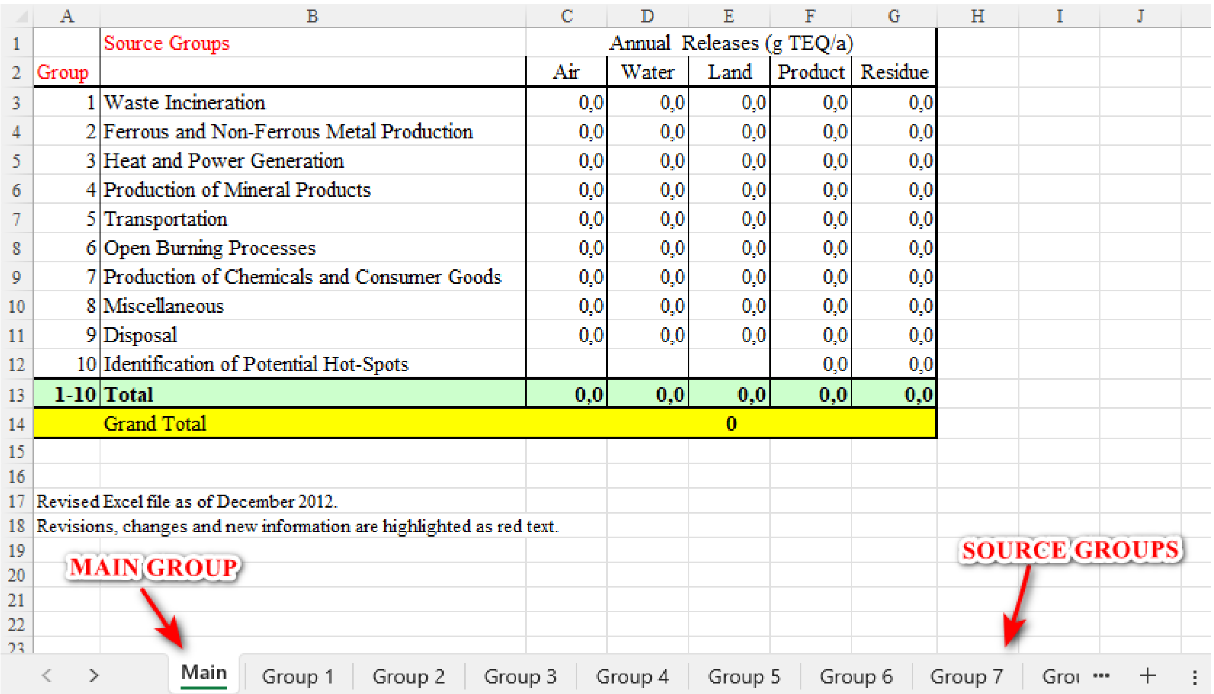


Figure 1. Location of the study area

Emission factors: Quantity of dioxins and furans expressed in grams per toxic equivalent per unit of activity (g TEQ / t) emitted by a class of activity towards a vector.

Activity rate: Annual quantity of product manufactured (steel, compost, etc.) or raw materials transformed (incinerated hazardous waste, diesel, etc.), or even materials released (m^3 of combustion gas, liters of waste water, etc.) in a class/category/activity source.

The sum of all these calculations gives the total releases for a given source (source intensity) per year. Ten groups of sources formed from the defined categories (**Figure 2**).



Group	Source Groups	Annual Releases (g TEQ/a)				
		Air	Water	Land	Product	Residue
1	Waste Incineration	0,0	0,0	0,0	0,0	0,0
2	Ferrous and Non-Ferrous Metal Production	0,0	0,0	0,0	0,0	0,0
3	Heat and Power Generation	0,0	0,0	0,0	0,0	0,0
4	Production of Mineral Products	0,0	0,0	0,0	0,0	0,0
5	Transportation	0,0	0,0	0,0	0,0	0,0
6	Open Burning Processes	0,0	0,0	0,0	0,0	0,0
7	Production of Chemicals and Consumer Goods	0,0	0,0	0,0	0,0	0,0
8	Miscellaneous	0,0	0,0	0,0	0,0	0,0
9	Disposal	0,0	0,0	0,0	0,0	0,0
10	Identification of Potential Hot-Spots				0,0	0,0
1-10	**Total**	**0,0**	**0,0**	**0,0**	**0,0**	**0,0**
	Grand Total			0		

Revised Excel file as of December 2012.
Revisions, changes and new information are highlighted as red text.

Figure 2. Emissions factors and calculation

3. Results and Discussion

3.1 Identification of sources activities

The visit to the integrated agricultural unit of Zuénoula made it possible to identify the areas of production of persistent organic pollutants recorded in **Table 1**.

Table 1. List of source activities

List of identified activities likely to generate POPs	Uncontrolled combustion processes (burning of standing cane)
	Bagasse incineration
	Light fraction incineration
	Fuel reserve station

3.1.1 Burning of standing cane

This process involves burning sugar cane fields before and after harvest. This helps destroy weeds, scare away venomous and dangerous animals, facilitate cleaning of the land and reduce the proliferation of parasites (**Figure 3**). Although this practice is widespread in Côte d'Ivoire, it can cause air pollution and soil degradation. The smoke released may contain fine particles and toxic gases such as dioxins and furans, which are harmful to the environment and human health.

Figure 2. Uncontrolled combustion process

3.1.2 Bagasse incineration

Bagasse is the fibrous residue that remains when sugar cane is crushed to extract its sweet juice. It constitutes approximately 30% of the total weight of sugar cane. Bagasse is primarily used as fuel in boilers during sugar refining, providing the thermal energy needed for the process. In addition, it makes it possible to generate part of the electricity used by the sugar factories using steam generators (**Figure 4**). The downside is that sweets release carbon dioxide into the atmosphere. Also, the bagasse incineration process also causes emissions of dioxins and furans.

Figure 4. Factory showing the bagasee shed (A) and the two boilers (B)

3.1.3 Burning of light fraction (bags and packaging) for manufacture of paving stones

In the production of sugar cane, various phytosanitary products packaged in plastic packaging are used. The latter are rejected as waste after use. All these used objects (packaging, plastic bags, helmets, etc.) are recycled. This recycling consists of transforming this plastic waste (by incineration with the addition of sand) into floor covering material such as paving stones. The large quantity of plastic incinerated shows that this manufacturing process is a potential source of generation of persistent pollutants in the environment (**Figure 5**).

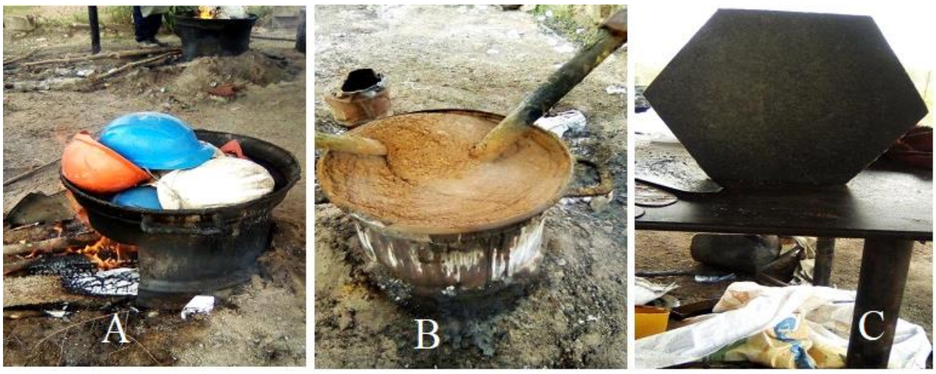


Figure 5. Recycling of plastic waste (A : incineration of plastics ; B : addition of sand; C : finished « pavement » product)

3.1.4 Fuel reserve station

The fuel tank station was considered a potential source of unintentional POPs due to the fact that it is the fueling point for all the unit's engines (**Figure 6**). During the operation of these engines (factory, vehicles, machinery), an internal combustion process is initiated which will subsequently be the source of atmospheric emissions.

3.2 Characterization of different unintentional POPs in the environment

To characterize POPs using Toolkit 2013, you must first identify the source group, then know the category to which the mentioned activity belongs and finally select the class that refers to it. Among the activities mentioned, bagasse incineration and light fraction burning belong to group 1, waste incineration. The burning of standing cane is classified in group 6 corresponding to uncontrolled combustion processes. The fuel reserve station belongs to group 5, i.e. the transport group.

Figure 6. Fuel storage station

3.2.1 Characterization at the level of waste incineration

The incineration of 24,436 tonnes of light fraction waste provides a quantity of 24,436 gTEQ/year of emissions of dioxins and furans into the air while that of bagasse (146,294 tonnes) emits 1,463 gTEQ/year. On the other hand, a zero quantity is emitted in the other environmental matrices for these two sources. Therefore, the incineration of waste produces overall in the air, 25,899 gTEQ/year of dioxins and furans, a zero quantity in the ground, water, products and 1.5 gTEQ/year in the ashes (**Figure 7**).

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1				Source categories	Potential Release Route (µg TEQ/t)						Production	Annual release					
2									Residue		t/a	g TEQ/a	g TEQ/a	g TEQ/a	g TEQ/a	g TEQ/a	g TEQ/a
3	Group	Cat.	Class		Air	Water	Land	Product	Fly Ash	Bottom Ash		Air	Water	Land	Product	Fly ash	Bottom Ash
4	1			**Waste incineration**													
5		a		**Municipal solid waste incineration**							0	0,000	0	0	0	0,000	0,000
6			1	Low technol. combustion, no APCS	3 500		NA	NA	0	75		0,000				0,000	0,000
7			2	Controlled comb., minimal APCS	350		NA	NA	500	15		0,000				0,000	0,000
8			3	Controlled comb., good APCS	30		NA	NA	200	7		0,000				0,000	0,000
9			4	High tech. combustion, sophisticated APCS	0,5		NA	NA	15	1,5		0,000				0,000	0,000
10		b		**Hazardous waste incineration**							0	0,000	0	0	0	0,000	0,000
11			1	Low technol. combustion, no APCS	35 000		NA	NA	9 000			0,000				0,000	0,000
12			2	Controlled comb., minimal APCS	350		NA	NA	900			0,000				0,000	0,000
13			3	Controlled comb., good APCS	10		NA	NA	450			0,000				0,000	0,000
14			4	High tech. combustion, sophisticated APCS	0,75		NA	NA	30			0,0000				0,000	0,000
15		c		**Medical waste incineration**							0	0,000	0	0	0	0,000	0,000
16			1	Uncontrolled batch combustion, no APCS	40 000		NA	NA		200		0,000				0,000	0,000
17			2	Controlled, batch, no or minimal APCS	3 000		NA	NA		20		0,000				0,000	0,000
18			3	Controlled, batch comb., good APCS	525		NA	NA	920	ND		0,000				0,000	
19			4	High tech, continuous, sophisticated APCS	1		NA	NA	150			0,000				0,000	0,000
20		d		**Light fraction shredder waste incineration**							**24 436**	24,436	0	0	0	0,000	0,000
21			1	Uncontrolled batch comb., no APCS	1 000		NA	NA	ND	ND	24 436	24,436					
22			2	Controlled, batch, no or minimal APCS	50		NA	NA	ND	ND		0,000					
23			3	High tech, continuous, sophisticated APCS	1		NA	NA	150			0,000				0,000	0,000
24		e		**Sewage sludge incineration**							0	0,000	0	0	0	0,000	0,000
25			1	Old furnaces, batch, no/little APCS	50		NA	NA	23			0,000				0,000	0,000
26			2	Updated, continuously, some APCS	4		NA	NA	0,5			0,000				0,000	0,000
27			3	State-of-the-art, full APCS	0,4		NA	NA	0,5			0,000				0,000	0,000
28		f		**Waste wood and waste biomass incineration**							**146 294**	1,463	0	0	0	1,463	0,000
29			1	Old furnaces, batch, no/little APCS	100		NA	NA	1 000			0,000				0,000	0,000
30			2	Updated, continuously, some APCS	10		NA	NA	10		146 294	1,463				1,463	0,000
31			3	State-of-the-art, full APCS	1		NA	NA	0,2			0,000				0,000	0,000
32		g		**Animal carcasses burning**							0	0,000	0	0	0	0,000	0,000
33			1	Old furnaces, batch, no/little APCS	500		NA	NA	ND	ND		0,000					
34			2	Updated, continuously, some APCS	50		NA	NA	ND	ND		0,000					
35			3	State-of-the-art, full APCS	5		NA	NA	ND	ND		0,000					
36	1			**Waste Incineration**								**25,899**	**0**	**0**	**0**	**1,463**	**0,000**
37																1,5	

Figure 7. Estimation of dioxins and furans at the level of waste incineration

3.2.2 Characterization at the transport level

POPs emissions from the transportation sector are caused by incomplete combustion of fuel in engines. The emission levels of these pollutants in vehicle exhaust gases depend on many factors, such as the type and state of maintenance of the engine, the type and quality of the fuel, the climate, etc. To develop a PCDD/PCDF emissions inventory, a simple approach can be used where the emission rate is considered as a function of engine type and fuel type used as indicated in the Toolkit. For this establishment, the data collected will be assigned to a type of engine to make the estimate based on the annual quantity of fuel. To do this, a conversion factor was initiated estimating that one liter (L) of gasoline corresponds to 0.74 kg and that of diesel to 0.85 kg. After conversion of the data received, the agricultural unit had an annual consumption of 1,560 tonnes of fuel. The data inserted into the spreadsheet revealed a value of 0.003 gTEQ/year of atmospheric emissions (**Figure 8**).

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1				Source categories	Potential Release Route (µg TEQ/t)					Consumption	Annual release				
2	Group	Cat.	Class		Air	Water	Land	Product	Residue	t/a *	g TEQ/a	g TEQ/a	g TEQ/a	g TEQ/a	g TEQ/a
3	5			Transport							Air	Water	Land	Product	Residue
4		a		4-Stroke engines						1 560	0,003	0,000	0,000	0,000	0,000
5			1	Leaded fuel	2,2	NA	NA	NA	NA	1 560	0,003				
6			2	Unleaded gasoline without catalyst	0,1	NA	NA	NA	NA		0,000				
7			3	Unleaded gasoline with catalyst	0,001	NA	NA	NA	NA		0,000				
8			4	Ethanol with catalyst	0,0007	NA	NA	NA	NA		0,000				
9		b		2-Stroke engines						0	0,000		0	0	0
10			1	Leaded fuel	3,5	NA	NA	NA	NA		0,000				
11			2	Unleaded fuel	2,5	NA	NA	NA	NA		0,000				
12		c		Diesel engines						0	0,000	0,000	0,000	0,000	0,000
13			1	Regular Diesel	0,1	NA	NA	NA	ND		0,000				
14			2	Biodiesel	0,07	NA	NA	NA	ND		0,000				
15		d		Heavy oil fired engines						0	0,000	0	0	0	0
16			1	All types	2	NA	NA	NA	ND		0,000				
17	5			Transport							0,003	0	0	0	0

Figure 8. Quantification of dioxins and furans from transport emissions

3.2.3 Characterization at the level of uncontrolled combustion processes

This involves burning in the open air without defined or controlled conditions. Aeration of combustion occurs by natural ventilation. Unintentional releases of POPs with solid residues (combustion ash) are considered releases to land rather than residues for this source group. Without retention, ashes remain on the ground and are generally not collected for landfill. For the pre-harvest, 421,865 tonnes of cane were burned over an area of 86,882.73 hectares. This process generated emissions of dioxins and furans including 1.687 gTEQ/year in the air and 0.021 gTEQ/year at ground level (**Figure 9**).

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1				Source categories	Potential Release Route (µg TEQ/t)					Production	Annual release				
2	Group	Cat.	Class		Air	Water	Land	Product	Residue	t/a	g TEQ/a	g TEQ/a	g TEQ/a	g TEQ/a	g TEQ/a
3	6			Open Burning Processes							Air	Water	Land	Product	Residue
4		a		Biomass burning						421 865	1,687	0	0,021	0	0
5			1	Agricultural residue burning in the field of cereal and other crops stubble, impacted, poor burning conditions	30	ND	10	NA	NA		0,000		0,000		
6			2	Agricultural residue burning in the field of cereal and other crops stubble, not impacted	0,5	ND	0,05	NA	NA		0,000		0,000		
7			3	Sugarcane burning	4	ND	0,05	NA	NA	421 865	1,687		0,021		
8			4	Forest fires	1	ND	0,15	NA	NA		0,000		0,000		
9			5	Grassland and savannah fires	0,5	ND	0,15	NA	NA		0,000		0,000		
10		b		Waste burning and accidental fires						0	0,000	0	0,000	0	0
11			1	Fires at waste dumps (compacted, wet, high Corg content)	300	ND	10	NA	NA		0,000		0,000		
12			2	Accidental fires in houses, factories	400	ND	400	NA	NA		0,000		0,000		
13			3	Open burning of domestic waste	40	ND	1	NA	NA		0,000		0,000		
14			4	Accidental fires in vehicles (per vehicle)	100	ND	18	NA	NA		0,000		0,000		
15			5	Open burning of wood (construction/demolition)	60	ND	10	NA	NA		0,000		0,000		
16	6			Open Burning Processes							1,687	0	0,021	0	0,000

Figure 9. Quantification of dioxins and furans in uncontrolled combustions

The estimation of unintentional persistent organic pollutants made it possible to know the quantity of dioxins and furans released into the environment of the integrated agricultural unit of Zuénoula which is a Classified Installation for Environmental Protection (ICPE). These results (summarized in

Table 2) showed potential generating sources of persistent pollutants. Note that emissions at the level of certain groups and/or matrices have been neglected due to their low rejection rate.

Table 2. Summary of the estimation of releases of dioxins and furans

Groups	Source groups	Annual emissions (g TEQ/a)				
		Air	Water	Ground	Products	Residues
1	Waste incineration	25.9	0,0	0,0	0,0	1,5
2	Production of ferrous and non-ferrous metals	0.0	0,0	0,0	0,0	0,0
3	Electricity production and heating	0.0	0,0	0,0	0,0	0,0
4	Production of meneral products	0.0	0,0	0,0	0,0	0,0
5	Transport	0.0	0,0	0,0	0,0	0,0
6	Uncontrolled combustion processes	1.7	0,0	0,0	0,0	0,0
7	Production and use of chemicals and consumer goods	0.0	0,0	0,0	0,0	0,0
8	Divers	0.0	0,0	0,0	0,0	0,0
9	Elimination	0.0	0,0	0,0	0,0	0,0
10	Identification of potential black spots				0,0	0,0
1-10	Total	27.6	0,0	0,0	0,0	1,5
	Overall total emissions	29.1				

3.3 Discussion

This study was carried out with the aim of estimating persistent organic pollutants in order to propose measures to improve discharges from the integrated agricultural unit of Zuénoula. To do this, it was necessary to identify the different activities that are sources of persistent organic pollutants at the industrial unit level.

As such, the open-air burning of cane plantations before harvest, the fuel storage station, the bagasse incineration processes to feed the boiler and the plastic incineration processes for the manufacture of materials floor covering (pavers), are the activities identified as potential sources of Unintentional POP. These results corroborate those of (Ouédraogo, 2023) which show that industrial processes, energy production, and the incineration of plastic waste are at the origin of the emission of persistent organic pollutants, precisely dioxins and furans (PCDD/PCDF). It was found that combustion processes are the center of all PCDD/PCDF producing activities at the industrial unit level.

This finding is similar to that of (Zubair, 2019) who stated that dioxins and furans are contaminants that are released into the environment through combustion processes.

The characterization of emissions of persistent pollutants in environmental matrices was done through the groups identified in the toolkit, namely waste incineration (group 1), transport (group 5), uncontrolled combustion processes (group 6). In group 1, the incineration of 24436 tonnes of plastics gave a quantity of 24,436 gTEQ/year of dioxins and furans in the air and a zero quantity in other environmental matrices. Still in the same group, the incineration of 146294 tonnes of bagasse produced an emission of 1,463 gTEQ/year of dioxins and furans in the air and 1,5 gTEQ/year in the residues, a zero quantity in the other matrices. In total, the emissions of these pollutants in this group 1 were estimated at 25,899 gTEQ/year in the air and 1,5 gTEQ/year in residues. At the transport level (group 5), 1560 tonnes of fuel were burned, resulting in releases of dioxins and furans estimated at 0,003 gTEQ/year in the air and zero quantity in other environmental matrices. As for group 6, 421865 tonnes of cane were burned in the fields producing releases of dioxins and furans estimated at 1,687 gTEQ/year in the air and 0,021 gTEQ/year in the soil. These results could be explained by the fact that, in certain environments, releases were not predicted for these environments or due to the absence of emission factors in the assessment tool. In summary, the characterization of emissions of dioxins and furans into the environment within the industrial unit gave 27,6 gTEQ/year of emissions into the air and 1,5 gTEQ/year into residues mainly in the fly ash and a zero quantity in other environmental matrices (water, soil and products). These results would be due to the fact that at the level of certain matrices (soil) emissions were considered negligible by the toolkit due to the small quantity of their emissions. Total emissions of dioxins and furans from the integrated agricultural unit of the Sucrivoire company in Zuénoula into the environment were estimated at 29,1 gTEQ/year. Air is the environmental matrix most impacted by these emissions. These observations are in the same direction as the results of (Mekhous *et al*., 2011) who estimated the emissions of dioxins and furans into the air at 2,8 gTEQ/year in the incineration of municipal waste at only a quarter of the waste considered. These emissions would be greater if the total quantity was taken into account.

In view of the results of the study, it is proposed to the integrated agricultural unit to regulate the combustion temperature beyond 800 °C according to the requirements of the Stockholm Convention (2001) in order to reduce dioxin emissions and furans. These observations agree with those of (Sibile *et al*., 2021) who recommend maintaining the post-combustion temperature at more than 800 °C. The monitoring of emissions of these pollutants must be regular due to their persistent and persistent nature (Denhez, 2011). They are very resistant and tend to accumulate along the food chain (Bodiguel *et al*., 2011), (Sullivan and Sandau, 2014). (POPs) are associated with a wide range of toxic effects on human health and wildlife (Mehmetli and Koumanova, 2007).

Conclusion

The objective of this work is to estimate persistent organic pollutants with the aim of proposing measures to improve these discharges. The results made it possible to identify the different activities generating POPs within the industrial unit. These include combustion activities such as waste incineration, transport and burning of cane plantations before harvest. In terms of characterization, it appears that the matrix most impacted by persistent organic pollutants (dioxins and furans) is air with 27,6 g, the others being little or not impacted. In view of these results, it was proposed to regulate the combustion temperature beyond 800°C in order to reduce emissions of dioxins and furans within the industrial unit. The monitoring of emissions of these pollutants must be regular due to their persistent and persistent nature.

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