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Chlordecone consumption estimated by sewage epidemiology approach for health policy assessment

Damien A. Devault¹ · Laurence Amalric² · Sébastien Bristeau²

Abstract

Chlordecone is an organochlorine insecticide that was intensively used in the French West Indies to control the black weevil *Cosmopolites sordidus* in bananas. Its usage, however, resulted in the widespread pollution of the environment with heavy sanitary and social consequences, leading to population exposure mainly through food. Time-consuming and costly programs have been used to tackle this problem, and this study proposes to use the emerging sewage epidemiology approach to evaluate the current situation and the effect of such programs. The results determine the maximal value of chlordecone consumption, and considering the detection limit of the analytical protocol, the wastewater was found to have undetectable amounts of chlordecone. This value confirms the efficiency of the population protection strategy provided by French sanitary and environmental authorities. It also bolsters the usage of sewage epidemiology in pesticide assessment and relativizes the chlordecone risk compared to other chemicals of lesser concern.

Keywords Kepone · Back-calculation · Population exposure · French West Indies · Martinique

Abbreviation

ADI	Admissible daily intake
BOD ₅	Biochemical oxygen demand over 5 days
CLD	Chlordecone
CLD5BH	5b-Hydrochlordecone
CLDOH	Chlordecol
CLD-C13	CLD isotope-labelled
DTR	Drug target residue
FWI	French West Indies
GC-MS/MS	Gas chromatography-tandem mass spectrometer
LD	Limit of detection
NOAEL	No observed adverse effect level
PE	Population equivalent

THC	Δ-9-Tetrahydrocannabinol
THC-COOH	11-nor-Δ-9-Carboxytetrahydrocannabinol
WWTP	Wastewater treatment plant

Introduction

Pesticide contamination of humans and ecosystems has become a major environmental concern. The impact of these products on human health and ecosystem integrity has been extensively studied, especially for persistent pesticides (Bro-Rasmussen 1996), but research is still necessary to evaluate the effects of mixtures in particular. Ecosystem contamination resulting from agricultural practices has been the subject of many studies, but for the majority of persistent organic pollutants (POPs), field or laboratory metabolisation studies are hindered by the very long half-lives of the compounds under investigation. The environmental management of the impact of such compounds is driven by POP half-life: either dilatory solutions should be found while waiting for a decrease in contamination or the professional sectors condemned by the persistent, high-level contamination of the environment should change. The latter alternative is involved in the case of chlordecone in the French West Indies (FWI) (Dubuisson et al. 2007).

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Chlordecone (CLD, or Kepone) is an organochlorine insecticide that was applied to fight black weevil *Cosmopolites sordidus* infestation of banana plantations from 1972 to 1978 and then from 1981 to 1993 in the FWI. CLD has also been used in Europe, the USA, Africa, and Latin America (Le Déaut and Procaccia 2009). The total mass of CLD (ca 300 tons) spread across 190 km² in Martinique and Guadeloupe (FWI) led to the severe contamination of soils (Cabidoche et al. 2009), surface and ground water (respectively, Bocquené and Franco 2005 and Gourcy et al. 2009), plant products (Cabidoche and Lesueur-Jannoyer 2012), seafood (Coat et al. 2006, 2011), and livestock (e.g. Jondreville et al. 2014). Further, Mirex, an insecticide used more frequently worldwide than CLD (Hodgson 1998; Kaiser 1978), is expected to turn into CLD by photolysis (Alley et al. 1974; Ivie et al. 1974). CLD contamination has also been reported in coral fish in French Polynesia (Roche et al. 2011) and in *Chiloscyllium plagiosum* sharks fished near Hong Kong (Cornish et al. 2007). This would suggest that CLD could be much more widely distributed around the planet than initially thought. This environmental challenge needs to be tackled, but especially in the FWI since one sixth of the total 1800 tons of CLD ever produced in the world was spread across several thousand hectares in Martinique and, to a lesser extent, in Guadeloupe in the Caribbean until the mid-1990s. Such usage has led to acute pollution evoked in the scientific literature since 2000.

The sanitary potential impact on the local population identified to date notably includes an increased risk of prostate cancer (Multigner et al. 2010), negative effects on the cognitive and motor development of 7-month-old infants (Dallaire et al. 2012), and increased risk of preterm birth. Contrary to the historical contamination that occurred at the CLD production plant in Hopewell where Kepone disease was due to worker exposure, the main exposure expected in the FWI is linked to food and not to occupation. The acute sanitary, environmental, economic, and social impact of CLD pollution in the FWI has led to limitations or bans on established economic and traditional activities (Joly 2010). The aim of this article is to determine whether this prophylactic strategy has effectively protected the population.

To provide short-term data that is obtained concomitantly with drug consumption, Zuccato et al. (2005, 2008) developed an estimation method based on the measurement of drug residues in wastewater, which allows for the subsequent back-calculation using metabolism data. Currently, the prevalence of illicit substance consumption in the population is mainly estimated based on population surveys, seizure data, and inquiries, but these indirect methods are imprecise, time-consuming, and limited by the intrinsic inadequacies of the investigation tools (Devault et al. 2014). Furthermore, the results are usually published 1 year after data collection. These shortcomings all complicate the reactivity of the public authorities

(Daughton 2011). Studies have already shown significant differences in the consumption of illicit drugs between countries, but the innovative dimension of this approach is now being focused on pesticides (Rousis et al. 2017). Nevertheless, the biocide use, runoff, and lixiviation of contaminated soils could interfere in the analysis. Thus, in the present study, the investigated catchment area was selected because soils and groundwater are not contaminated, and the possibility of confusing inlet is null (Baran and Arnaud 2013). Anything measured in the study is due to human ingestion of CLD through consumption of local produce and water.

To our knowledge, this study is the first to provide an estimation of the sewage concentration of CLD. The back-calculation was performed on CLD, because it is known to be toxicokinetic in human bodies (Faroon et al. 1995). Consumption was estimated using the sewage epidemiology method with CLD taken as the drug target residue (DTR), given that CLD is mostly not degraded in the human body (Faroon et al. 1995). The wastewater treatment plant (WWTP) catchment area in Martinique chosen for this study did not have any past or present banana plantations or any animal husbandry and slaughter activities, considering that animal excretions could be contaminated by CLD (Lastel et al. 2016) and confused with that of humans. The groundwater of this area was likewise free from CLD, because of its land use. Further, the area was not affected by tourist accommodation. Other factors will be discussed below such as the technical differences in sewage management and their impact on the back-calculation used in the sewage epidemiology approach.

The acceptable daily intake (ADI) of CLD is 0.5 µg/kg body weight/day for chronic exposure and 10 µg/kg body weight/day for acute exposure, i.e. respectively 100 times less than the no-observed-adverse-effect-level (NOAEL) (Faroon et al. 1995).

Materials and methods

Investigation site

Fort-de-France city urban area, Martinique, has a population of 110,000 inhabitants, and sewage from the entire urban area is sent to four WWTPs. However, in such rugged terrain, only half the population is connected to the sewerage system, i.e. around 50,000 inhabitants of the urban Fort-de-France area, meaning that a significant proportion of the population is not connected to the system, leading to wastewater discharge directly into the soil, rivers, and sea around the coral reef. Indeed, the WWTP catchment area selected for this study corresponds to the most connected population area. The sewer system, which is altered in Martinique on account of spontaneous uncontrolled urban sprawl, seismic activity, and human alterations such as illegal rainwater connections to collect and channel rain to the sewer network, is efficiently controlled in this residential

urban catchment area populated by the middle class with a number of high-income households. The district has already been successfully monitored and was selected for the present article because of its suitability (Devault et al. 2014, 2016b).

To link chemical consumption to a population, it is necessary to know the population size in the WWTP catchment area. Numerous models use hydrochemical parameters to calculate population size (Andreottola et al. 1994) instead of designed capacity. The estimated population based on the biochemical oxygen demand over 5 days (BOD₅) reported over last year is about 19,000 inhabitants for the selected WWTP with a maximal capacity that is four times greater. During the experiment, BOD₅ was calculated each day by properly adjusting the consumption to the associated population.

Sampling strategy

Raw wastewater sampling was conducted daily for 1 week from 1 to 7 July 2017 at the entry of the selected WWTP. Sampling was done using refrigerated autosamplers (Endress and Hauser ASP2000; Boissy-Saint-Léger, France) positioned before the bar screen to obtain 24-h flow-weighted composite influent samples with a sampling frequency at least six times per hour according to the local WWTP procedures. At the end of each sampling day, 600 mL of each sample was collected in a glass bottle with Teflon seal and transported in a cooler for immediate storage at -20 °C in the Martinique University laboratory, located 20 min from Aimé Césaire airport (Martinique). At the end of the sampling campaign, all frozen samples were transported by airplane carrier to the analytical laboratory of the Bureau de Recherches Géologiques et Minières (Orléans, mainland France).

Analytical methods

Chemicals

The standard chlordecone hydrate (CLD; 8% water) also named chlordecone gem-diol (CAS 143-50-0) and chlordecol isotope-labelled (no CAS number) (CLDOH-d1) are commercially available by Cil Cluzeau (Sainte-Foy-La-Grande, France). The standard chlordecol (CLDOH) (CAS 1034-41-9) is commercially available by Azur isotope (Marseille, France). The individual standards (CLD, CLDOH, and CLDOH-d1) were prepared from solid standards dissolved in acetone (200 mg/L) and stored at -18 °C. 5b-Hydrochlordecone (CAS 53308-47-7) at 10 mg/L in nonane and CLD isotope-labelled (CLD-C13) at 100 mg/L in nonane are commercially available by LGC Standards (Molsheim, France). All of these standards have purity greater than 98%. Analytic-grade organic solvents (acetone, cyclohexane, and hexane) were obtained from Fisher Scientific (Illkirch, France).

Liquid-liquid extraction

The pH of the completely thawed sample was adjusted to 2.5 using H₂SO₄ solution and spiked with two internal standards of CLD-C13 and CLDOH-d1 solution (0.5 mL each at 0.3 mg/L for 500 mL sample). A mass of 25 g NaCl was added, and the sample was blended with 30 mL of hexane/acetone mixture (85/15, v/v) for 10 min shaking. The organic phase was removed, and the solvent addition was repeated twice.

For raw wastewater, the water volume was reduced to 100 mL and diluted to 500 mL with bottled spring water to avoid emulsion formation and to optimise the separation of organic and aqueous phases. The final extract was 1 mL.

The extract was first frozen for 1 h to eliminate water traces, then concentrated to 0.5 mL using a TurboVap® LV Concentration Evaporator (Biotage, Uppsala, Sweden) at 40 °C and 0.6 bar, and finally solvent-exchanged to cyclohexane.

The method has been validated in natural water samples using different surface waters. Surface waters were enriched with their own sediment (dried at 40 °C, ground a homogenised) up to 500 mg/L. The organic carbon concentration in sediment was 5.5 g/kg. Then samples were spiked with the three compounds at two concentration level (0.1 and 0.3 µg/L for each compound) and extracted after 24 h contact time, to determine the recoveries. Complementary tests were done by enriching ground water with two contaminated soils from West Indies (after grinding) to check the liquid/liquid method efficiency (Fig. 1).

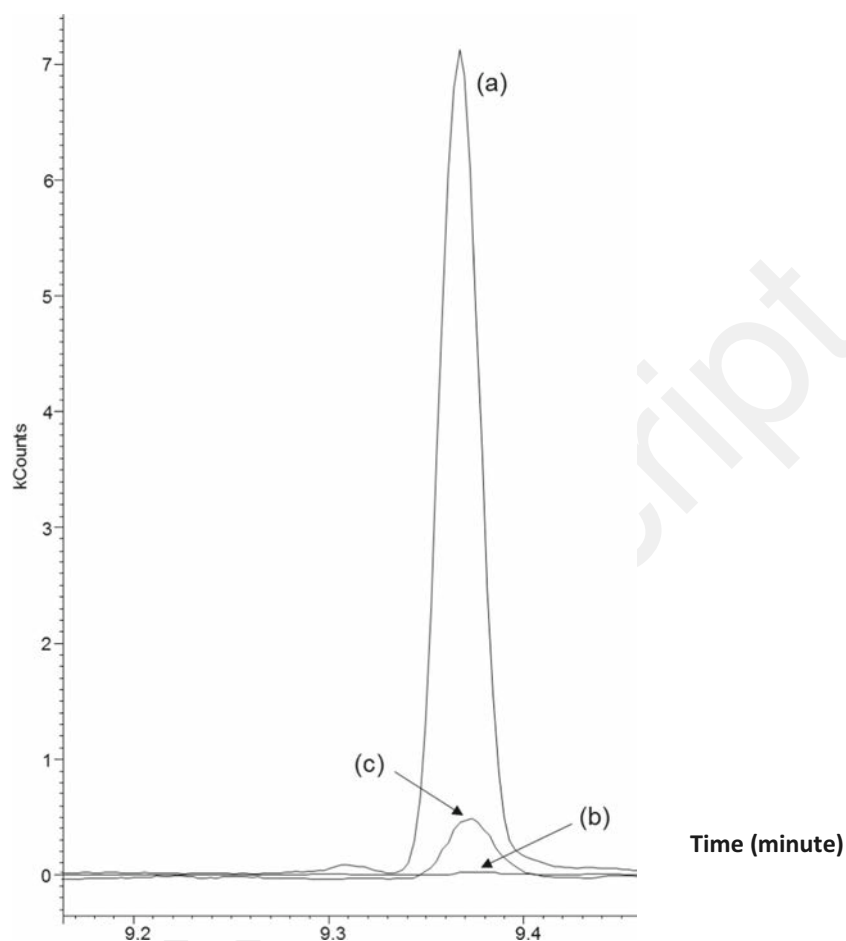
Recoveries are indicated in Figs. 2, 3, and 4.

Internal standards are used and added at the beginning of the protocol, to take into account the nature of the samples. It is imperative to correct the analytical variability and thus improve the precision and accuracy of the results. It should be added before sample extraction to suppress possible side effects during its analysis (loss during process, matrix effect, etc.). We chose internal standard with similar chemical and physical properties to match those of the analyte of interest, and labelled analogues as it is recommended. CLD-C13 and CLDOH-D1 are added in each sample and allow mimicking as closely as possible the behaviour of CLD and CLDOH, respectively. In order to quantify CLD5BH, a closely related compound CLD-C13 was used.

GC-MS/MS measurement

Extracts were analysed with GC-MS/MS using a GC 450 gas chromatography apparatus equipped with an 1177 injector, a Combi Pal (CTC) autosampler, and a 300-MS triple quadrupole mass spectrometer (Bruker, Marne la Vallée, France). The injector was equipped with a 4 × 6.3 × 78.5-mm liner with fibreglass and Sky™ deactivation (Restek, Lisses, France) operated in splitless mode at 280 °C and 1 mL/min. The column, an Rxi-1MS (30 m, 0.25-mm ID, 0.25 µm) from Restek,

Fig. 1 Chromatograms of CLD (a) CLD standard at 0.1 $\mu\text{g/L}$, (b) wastewater extract, and (c) wastewater extract spiked with CLD at 0.1 $\mu\text{g/L}$



was heated to 50 $^{\circ}\text{C}$ for 1.1 min, then to 250 $^{\circ}\text{C}$ at a gradient of 30 $^{\circ}\text{C}/\text{min}$, and finally to 310 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$ and isothermally for 1.5 min. The transfer line was at 310 $^{\circ}\text{C}$. The ionisation source, using electron ionisation at 70 eV to produce positive

ions, was at 250 $^{\circ}\text{C}$. The collision gas pressure (argon in CID) was 1.5 mTorr.

For quantitation purposes, data from the analysis standards from 15 to 3000 $\mu\text{g/L}$ were used to plot a weighted linear

Fig. 2 Chlordecone recovery from solid phase by liquid-liquid extraction (%). Yellow: for spiked suspended matters at 0.1 $\mu\text{g/L}$ for a $\pm 35\%$ uncertainty. Orange: for spiked suspended matters at 0.3 $\mu\text{g/L}$ for a $\pm 20\%$ uncertainty

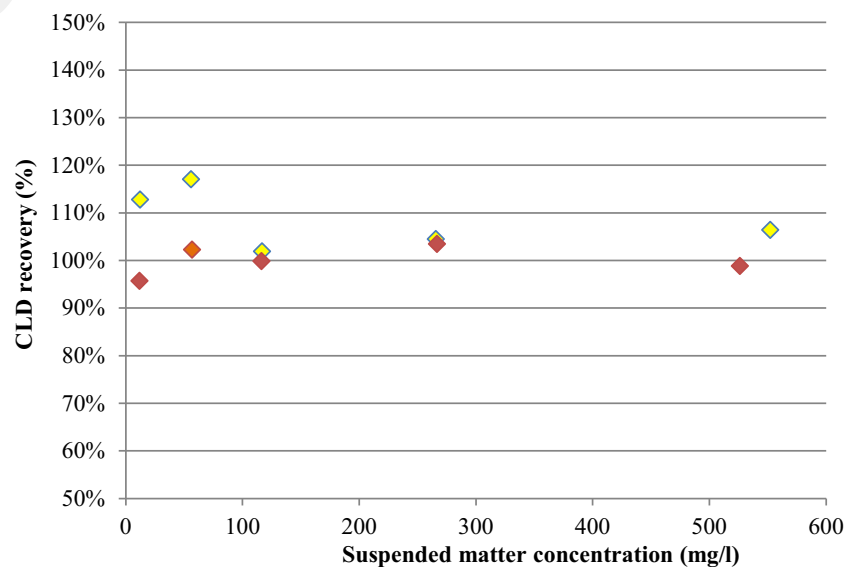
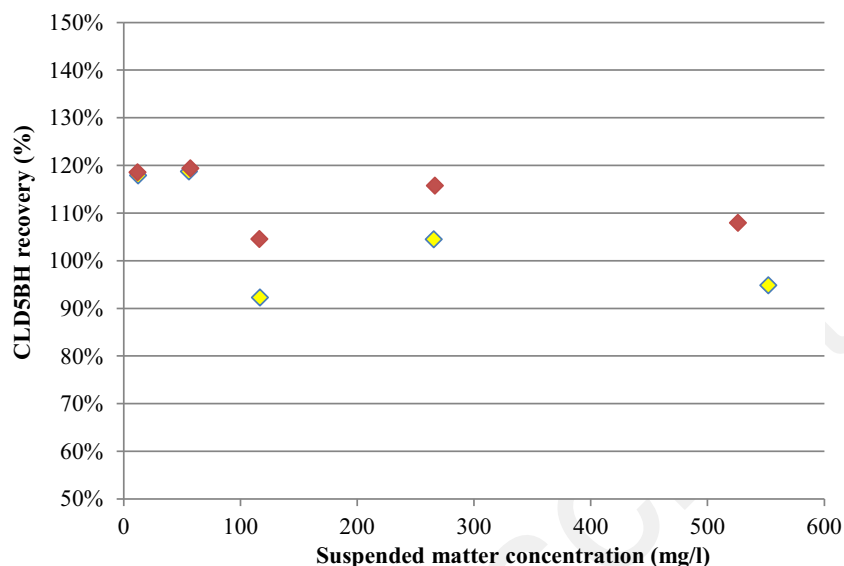


Fig. 3 5b-Hydrochlordecone recovery from solid phase by liquid-liquid extraction (%). Yellow: for spiked suspended matters at 0.1 µg/L for a ± 20% uncertainty. Orange: for spiked suspended matters at 0.3 µg/L for a ± 20% uncertainty



calibration. CLD-C13 as the internal standard was used for CLD and 5b-hydrochlordecone, while CLDOH-d1 was used for CLDOH.

Calculation of chemical consumption

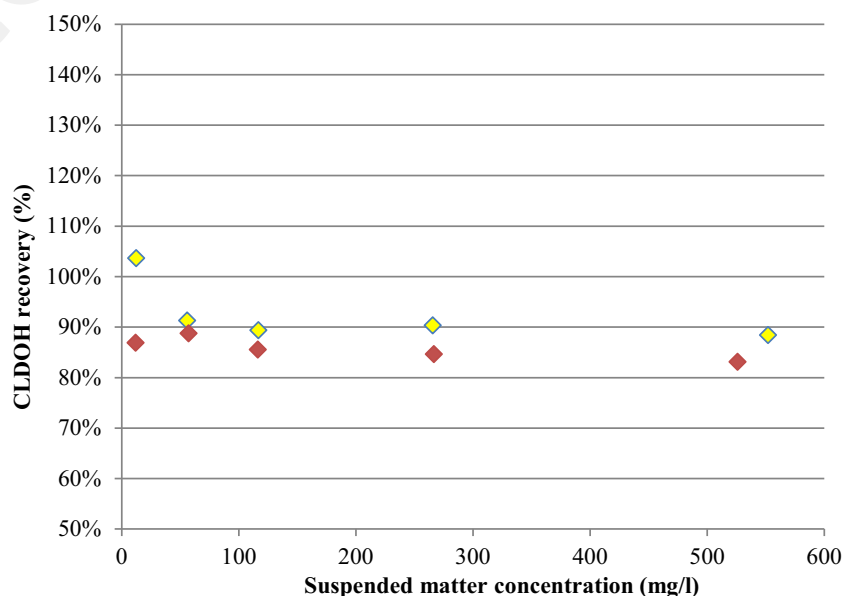
To conduct the back-calculation of consumption, the DTR must first be selected, followed by the excretion ratio (U_{ex}) of the DTR. DTR stability is a pivotal characteristic, as stressed by Devault et al. (2017).

The back-calculation was carried out using the following equation defined by Zuccato et al. (2008):

$$Q = \left(Q_{day} / U_{ex} \right) \times M_{ratio} / N_{inh} \quad (1)$$

Where Q is the consumption of molecule of interest (µg/inhabitant/day in the present article), Q_{day} is the load of the DTR calculated from the flow measurement and raw wastewater concentrations ($Q_{day} = \text{Flow} \times [\text{DTR}]$), U_{ex} is the percentage of the DTR excretion, M_{ratio} is the parent drug/DTR molar ratio (in this case $M_{ratio} = 1$ because CLD itself is DTR), and N_{inh} is the number of inhabitants in the catchment area. Stability data should be taken into account to prevent DTR degradation in sewage, but CLD is a strikingly stable compound, even if the analysis was performed with all the necessary caution. CLD is so stable that CLD degradation without human induction was previously regarded as impossible (Cabidoche et al. 2009), until Devault et al. (2016a) demonstrated indirectly its slow degradation in situ at least until 5b-hydrochlordecone strengthened by in vitro results of

Fig. 4 Chlordecol recovery from solid phase by liquid-liquid extraction (%). Yellow: for spiked suspended matters at 0.1 µg/L for a ± 30% uncertainty. Orange: for spiked suspended matters at 0.3 µg/L for a ± 25% uncertainty



corroborating studies (Chaussonnerie et al. 2016). Nevertheless, the time needed to turn CLD into 5b-hydrochlordecone seems to be out of range considering the human metabolism: experiments have shown that CLD excretion half-life is ranged between 97 and 177 days in humans (Adir et al. 1978; Cohn et al. 1978; Faroon et al. 1995; Multigner et al. 2016), although CLD is mostly changed under chlordecol form (80%) (Fariss 1980). Due to this prevalence, CLDOH is selected by authors as the DTR; Fariss also proposed an excretion rate of the total body burden of CLD per day (0.36%) but these values includes CLD and CLDOH, this last representing 80% of excreta. Monitoring CLDOH, the corresponding excretion rate is 80% of 0.36%, i.e. 0.288%.

However, sewage epidemiology is based upon the fully excretion of mother drugs and metabolites generated fast (e.g. 12 to 72 h): excretion rate and daily excretion rate are close even confounded. In the case of CLD, the canonical excretion rate of 0.36% implicates a fully excreted total body burden of CLD in 278 days. This value is not consistent with results of Cohn et al. (1978) who proposed 165 days as half-life in human body but Cohn et al. only focused on blood and fat when Fariss (1980) worked on broad sense excretion. Nevertheless, Fariss studied the excretion of rodents and compared it to humans as five times faster and signalled the reach of 80% of full excretion in 3 days under a first-order kinetic. In this way, and following Fariss (1980), (1) 80% of CLD excretion is reached in the 15 first days. (2) CLDOH being the DTR excreted a 80% of total body burden, the operational excretion rate, informing about the exposition of population during the last 15 days could be estimated as 4.26%.

$$\frac{P \times R}{N}$$

With P the percentage of excretion following a first-order kinetic, N the number of days corresponding to this first-order kinetic, and R the part of total body burden excreted under DTR form. Based on the limit of detection, the maximal input of CLD, i.e. the CLD consumption as if the consumption was at the limit of detection, was calculated, assuming that CLDOH concentration at the limit of detection is a way to show what the maximal extent of exposure would be when the method lacks the required level of sensitivity. The suitability of CLD as the DTR is discussed in “Chlordecone as DTR” section.

Results

The analytical result as summarised in Table 1

Paradoxically, the present monitoring did not present quantifiable CLD, CLDOH, or 5b-hydrochlordecone (CLD5BH) concentrations (below the limit of detection).

Table 1 Concentration in the wastewater samples (ng/L)

	Chlordecone	Chlordecol	5b-Hydrochlordecone
	(ng/L)	(ng/L)	(ng/L)
1 July	< LD	< LD	< LD
2 July	< LD	< LD	< LD
3 July	< LD	< LD	< LD
4 July	< LD	< LD	< LD
5 July	< LD	< LD	< LD
6 July	< LD	< LD	< LD
7 July	< LD	< LD	< LD

The back-calculated CLD expositions are summarised in Table 2a and b, with 0.288% as excretion rate and 4.26% respectively. The maximal input of CLD was estimated to be 86.8 or 5.87 $\mu\text{g}/\text{inhabitant}/\text{day}$, applying as excretion rate of 0.288 and 4.26%, respectively, based on 0.1 $\mu\text{g}/\text{L}$ as the limit of detection (LD) and considering the corresponding population equivalent. With 37,382 inhabitants equivalent the July 1, the population equivalent reaches a maximum very unusually high regarding the usual results for the studied WWTP (circa 20,000 inhabitant equivalent in average). Inversely, with 13,100 inhabitants equivalent the July 7, the population equivalent reaches a minimum unusually low regarding the usual results for the studied WWTP.

Discussion

The present article introduces chlordecol as a new DTR for chlordecone sewage epidemiology. The aim is to determine the efficiency of healthcare policy based on these sewage epidemiology results, notwithstanding the fact that CLDOH concentrations in the sampled wastewaters never reach the LD (Fig. 1). Indeed, this result should be interpreted as a daily concentration in wastewater between zero and close to the LD, even if it was never reached.

In the following discussion, the authors will study a worst-case scenario, i.e. when CLD concentration is close to the LD but without reaching it. Wastewater daily fluxes, being different each day, will be taken into account in order to provide an analysis that is as precise as possible.

The worst case of maximal CLD input was estimated to be 86.8 or 5.87 $\mu\text{g}/\text{inhabitant}/\text{day}$ based on 0.1 $\mu\text{g}/\text{L}$ LD, while no trace of CLD was observed in the sewage samples.

Chlordecone as DTR

Toxicokinetic data for CLD in human are available (Adir et al. 1978; Blanke et al. 1978; Boylan et al. 1979; Cannon et al. 1978; Cohn et al. 1978; Guzelian et al. 1981; Taylor 1982,

Table 2 Chlordecone maximal consumption based on limit of detection and flux evaluation. PE, population equivalent

	Volume (m^3 / day)	BOD ₅ (mgO_2 / L)	Population equivalent	M_{ratio}	Chlordecone U_{ex} (%)	Max flux ($\mu\text{g/day}$)	Exposure ($\mu\text{g} / \text{day} /$ inh)
(a)							
1 July	4078	550	37,382	1	0.288	407,800	≤ 37.9
2 July	3006	380	19,038	1	0.288	300,600	≤ 54.8
3 July	4195	300	20,975	1	0.288	419,500	≤ 69.4
4 July	4463	290	21,571	1	0.288	446,300	≤ 71.8
5 July	3616	280	16,875	1	0.288	361,600	≤ 74.4
6 July	4074	280	19,012	1	0.288	407,400	≤ 74.4
7 July	3275	240	13,100	1	0.288	327,500	≤ 86.8
(b)							
1 July	4078	550	37,382	1	4.26	407,800	≤ 2.56
2 July	3006	380	19,038	1	4.26	300,600	≤ 3.71
3 July	4195	300	20,975	1	4.26	419,500	≤ 4.7
4 July	4463	290	21,571	1	4.26	446,300	≤ 4.86
5 July	3616	280	16,875	1	4.26	361,600	≤ 5.03
6 July	4074	280	19,012	1	4.26	407,400	≤ 5.03
7 July	3275	240	13,100	1	4.26	327,500	≤ 5.87

1985). For animals, oral exposure data prevails, most of them for acute exposure (Blanke et al. 1978; Borzelleca and Skalsky 1980; Boylan et al. 1979; Cohn et al. 1978; Egle et al. 1978; Fujimori et al. 1982; Guzelian et al. 1981; Hewitt et al. 1986; Kavlock et al. 1980; Plaa et al. 1987; Richter et al. 1979; Skalsky et al. 1980; Wang et al. 1981).

CLD is absorbed through inhalation and ingestion in the gastrointestinal tract of humans and animals, then concentrated in the liver. During its long retention time in the body of few species including humans, CLD is metabolised to chlordecol.

CLD, chlordecol, and their glucuronide conjugates are slowly excreted mainly even only in the bile then the faeces (Blanke et al. 1978; Boylan et al. 1979; Cohn et al. 1978; Guzelian, 1981) but enterohepatic recirculation occurs. Considering sewer biocoenosis, the use of CLDOH appears to be the most reliable DTR, with an excretion rate of 72% added to 9% conjugated with glucuronic acid (Fariss et al. 1980; Guzelian, 1981), with more than 97% by faeces. CLD was not detected in sweat and only in minor quantities in urine (expected to 3% of excretion), saliva, and gastric juice (Cohn et al. 1978).

Only a very limited number of studies have examined the toxicokinetics of CLD through inhalation and dermal routes. Dermal absorption does occur, but to a limited extent (Hall et al. 1988; Shah et al. 1987), and it does not seem to occur more in the FWI. We found no studies on the distribution, metabolism, or excretion of CLD following dermal exposure. Occupational studies indicate that CLD is mainly absorbed through inhalation and ingestion, and in the case of the FWI, only the oral routes seem pertinent. We did not identify any animal data on the absorption, distribution, metabolism, and excretion of CLD following inhalation exposure. Regardless

of the conclusion of the present article, additional data (acute, intermediate, and chronic) for both humans and animals are needed to adequately compare the toxicokinetic parameters across all routes of exposure.

However, CLD estimation benefits of the experience acquired in sewage epidemiology, mainly for illicit drugs whose physico-chemical characteristics are consistent for CLD assessment (Δ -9-tetrahydrocannabinol (THC) congeners, 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine, methadone, respectively K_{OW} 6.5, 5.5, 4.2, to compare to CLD K_{OW} : 4.5). The CLD pattern in the sewer network is expected to be analogous to other molecules studied for sewage epidemiology.

Liquid-liquid extraction with hexane and acetone fully extracts CLD adsorbed on suspended matter until the suspended matter concentration reaches 500 mg/L (Fig. 2), i.e. a concentration never reached during this experiment.

Evaluation of the population exposure

The ADI of CLD is 0.5 $\mu\text{g/kg}$ body weight/day for chronic exposure and 10 $\mu\text{g/kg}$ body weight/day for acute ones. Considering the human conventional weight (60 kg), the ADI would be respectively 30 and 600 $\mu\text{g/inhabitant/day}$. However, only chronic exposure ADI is pertinent considering the CLD French West Indies context. The maximal estimated exposure based on our sewage epidemiology was between 86.8 and 37.9 $\mu\text{g/inhabitant/day}$ or between 5.87 and 2.56 $\mu\text{g/inhabitant/day}$ depending on the use of Fariss excretion rate or operational one described in "Calculation of chemical consumption", i.e. at least the range of ADI at least five times less than the CLD ADI for chronic exposure.

This maximal value should not be misunderstood, as it could induce an overestimation of the CLD consumption. Indeed, the value is calculated as the maximal daily intake per person, but there is no evidence that the real daily intake is 86.8 or 5.87 $\mu\text{g}/\text{inhabitant}/\text{day}$, respectively. The real daily intake is known to be between 0 and 86.8 or 5.87 $\mu\text{g}/\text{day}/\text{person}$, even if it is not possible to determine it precisely given the field results. This aspect highlights the next step in sewage epidemiology: lower quantification or detection limits could be allowed using passive samplers. Nevertheless, the population under investigation could still be exposed to CLD although at non-dangerous levels.

It is only possible to compare our results of CLD exposure to the literature with the pan-European analysis of Rousis et al. (2017) conducted in eight major cities in Italy, the UK, the Netherlands, Belgium, Spain, Denmark, and Norway, and performed on pre-emergent herbicides banned since 2003 (atrazine, simazine) as well as authorised pesticides whether used (terbuthylazine) or not (propazine). Such results are interesting because, like CLD, atrazine is persistent in the environment. Moreover, CLD is an insecticide, as the other pesticide exposures back-calculated by Rousis et al., i.e. pyrethroids and organophosphates.

Considering operational excretion rate results, i.e. Table 2b, CLD maximal exposure range is similar to the *s*-triazines and organophosphates observed by Rousis et al. (2017), lower than pyrethroids (range up to 125 $\mu\text{g}/\text{inhabitant}/\text{day}$) and much lower than alkyl phosphates (range up to 2000 $\mu\text{g}/\text{day}/\text{person}$). Permethrins ranged between 12 and 108% of ADI, while CLD maximal exposure ranged between 19.6% and 289% considering CLD ADI chronic exposure and “operational” excretion rate deducted from Fariss (1980) and adapted to sewage epidemiology, i.e. 4.26%, and the excretion rate directly proposed by Fariss (1980) corrected by CLDOH part, i.e. 0.288%.

Authors highlight also that results have been reached using a 0.1 $\mu\text{g}/\text{L}$ limit of detection, corresponding to a 0.3 $\mu\text{g}/\text{L}$ limit of quantification. Such analytical performance could be surpassed, including because protocol is primarily designed for surface water, not for wastewaters. Chlordecone analysis has been recently proposed with limit of detection two orders below the one reached in the present article.

Evaluation of sanitary framework results

The present study could be usefully compared to illicit drug consumption, which involves a willingly consumption of hazardous chemicals. Since 2013, the illicit drug consumption in the population connected to studied WWTP has been successfully monitored for SCORE (Sewage Analysis CORE group Europe) (Devault et al. 2014 and 2016b); cannabis and cocaine consumption reached 23,000 and 1300 $\mu\text{g}/\text{inhabitant}/\text{day}$, respectively. Even if the toxicological impact of each molecule should be taken into account, such previous works

on the sampled WWTP backs up the application to other molecules than illicit drugs.

The results of the present study could help to objectivise the sanitary efforts of the public authorities and provide guidance to decision makers regarding the critical level of illicit drug consumption in Martinique and the corresponding absence of a plan equivalent to the “chlordecone plans”. Indeed, the present results highlight the success of the “chlordecone plans” of the past decade, which have allotted 94 million euros to the CLD threat. To the best of the authors’ knowledge, CLD content in sludge has never been assessed.

It is worthwhile noting that the absence of CLDOH detection in the local sewage is a sort of evaluation of the sanitary efforts initiated to limit CLD use. Indeed, the present results show that sanitary and environmental managers have succeeded in preventing population contamination by conducting soil analysis and then limiting the cropping of roots and tubers in polluted areas and fishing in contaminated bays as well as by providing populations with safety instructions for suitable cooking and gardening. As the studied area is urban, housing rarely allows for significant-sized vegetable gardens, while informal markets could limit the need for supermarkets. That said, produce from both supermarkets and informal markets have been surveyed without highlighting prevalent contaminated food (2.7% of samples from Martinique, mainly from self-production in the contaminated area far from studied one). Moreover, the local context, understanding the spread of CLD (and subsequent pollution) as a contemptible colonial remnant, has helped to raise awareness and change behaviour (July 2010). Yet the same negative perceptions do not apply to illicit drug consumption, which obtains similar results pointing to the anecdotic consumption of illicit drugs. Tackling the drug problem will thus probably require more time, persuasion, and money.

Conclusions

Sum of CLDOH should be suitably used as a DTR in order to back-calculate the population exposure to this pesticide. Considering the area under investigation, the population exposure was demonstrated to be minimal and non-threatening. However, this study could be usefully extended to other areas, including contaminated area, ideally with better detection limit. In this study, sewage epidemiology was successfully applied to a propitious context regarding the stability of CLD, which lends support to the previous studies conducted in the same area.

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