

Biomonitoring research Zubieta 2021

Gipuzkoa Basque Country

Eggs
Sediment
Mosses

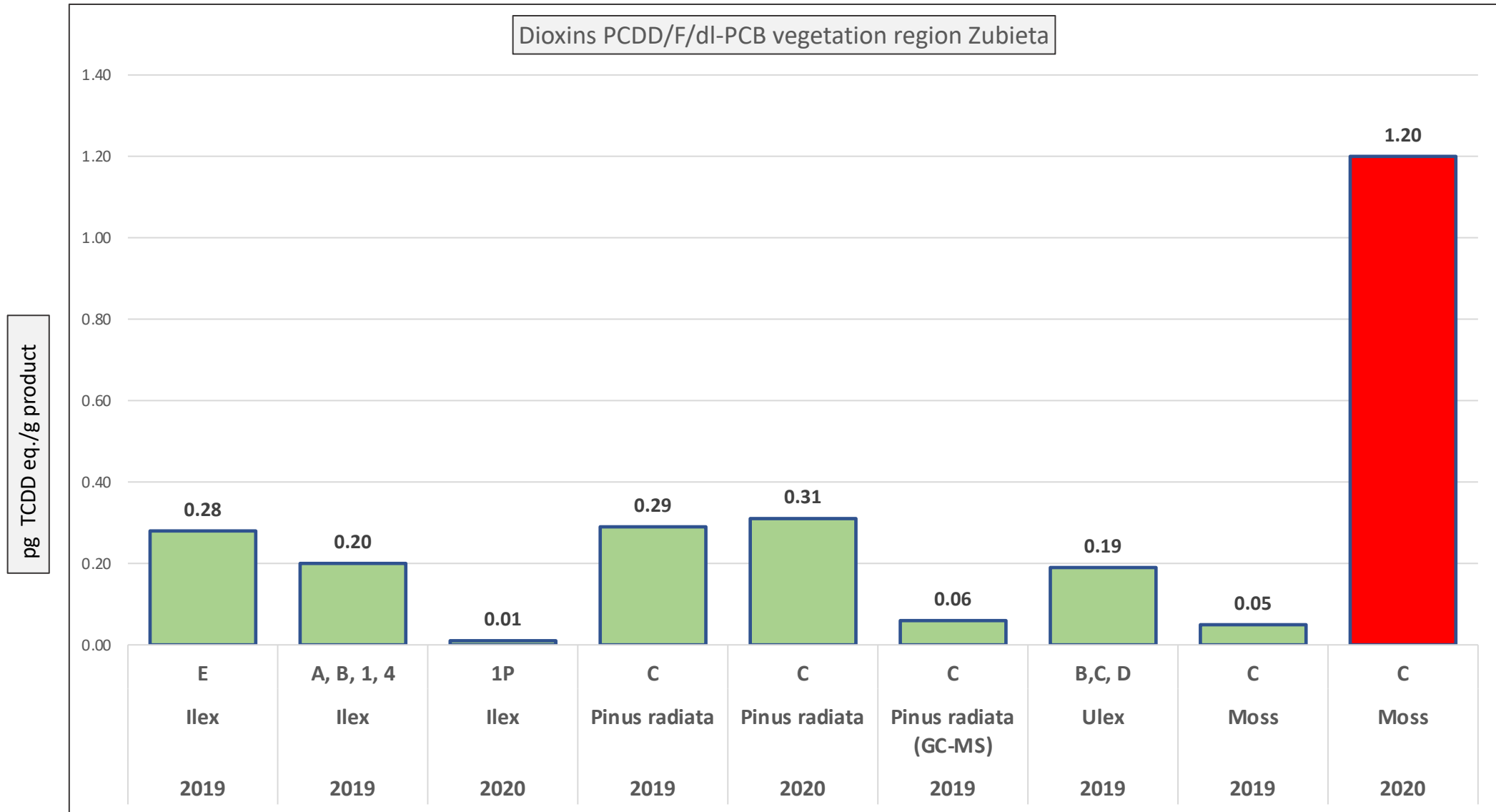


Key findings biomonitoring Zubieta 2021

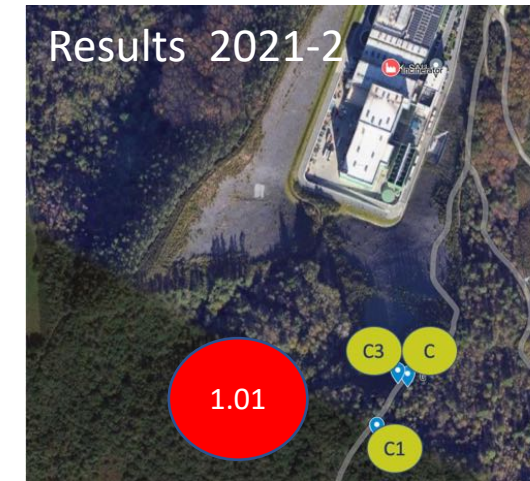
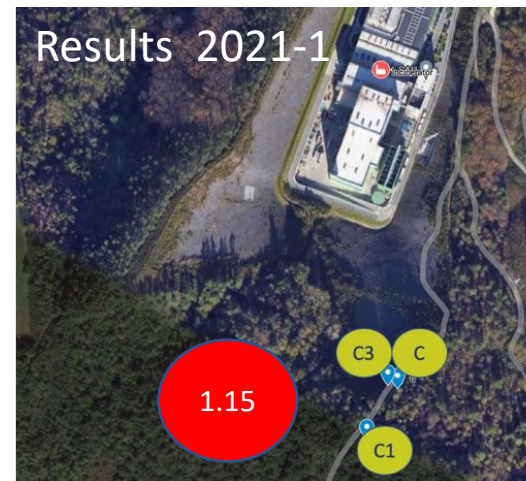
- High dioxin levels in mosses near the incinerator
- Elevated dioxins at egg location (3600 m) in the main wind direction south of the incinerator
- Typical combustion congeners, like OCDD and HpCDF1, are found in the eggs
- PFAS found in the biomatrices mosses, eggs and sediment
- More research is needed in water stream near incinerator, because of calamities



Reason for focus research 2021 on mosses



Increase dioxins in mosses in 2020



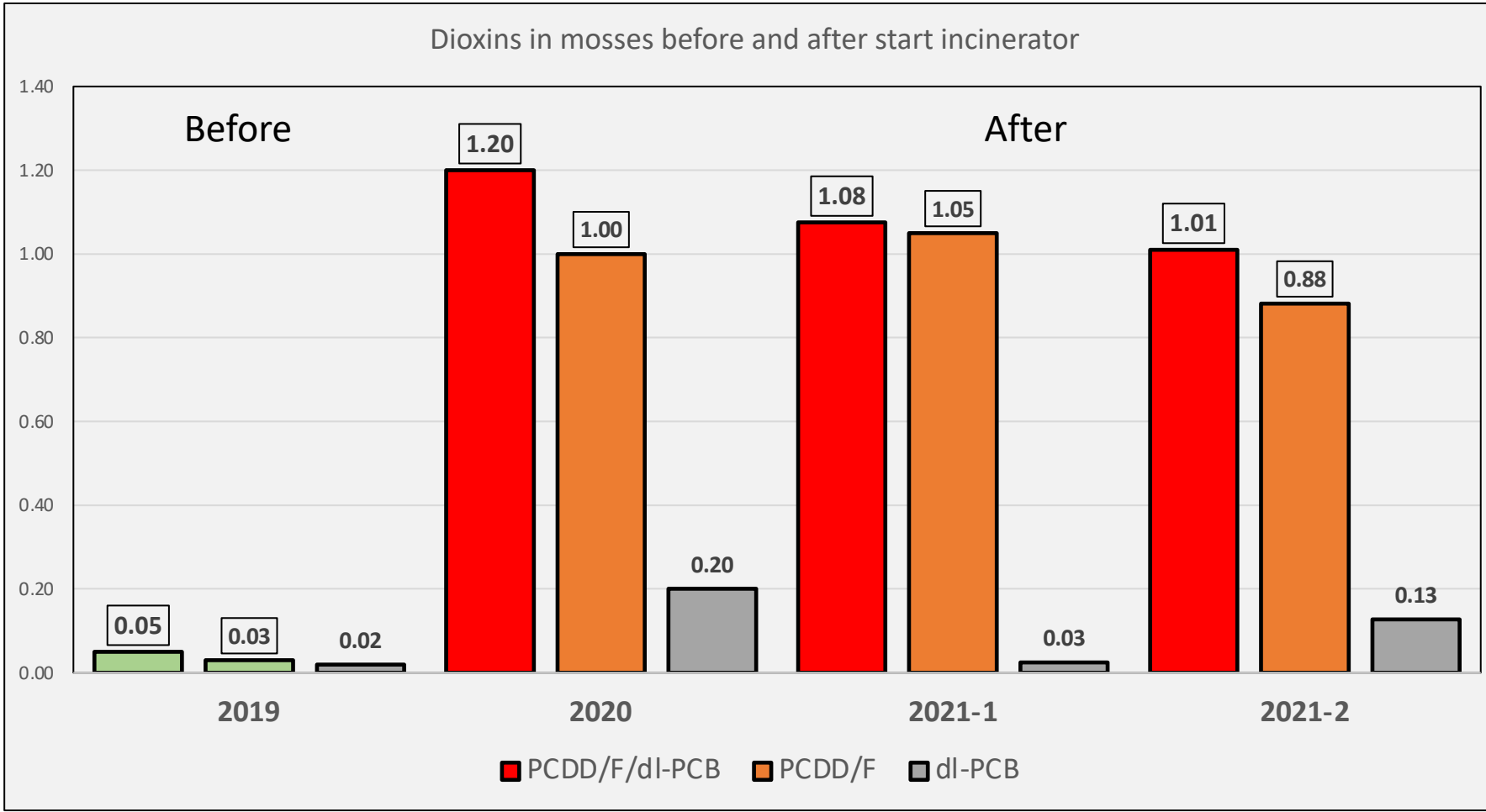
Zubieta biomonitoring mosses 2019 -2021 (MediumBound, MB)

				Distance		DR CALUX pg TCDD eq/g product		
	Date	Samle date	Number	(m)	Wind direction	PCDD/F/dl-PCB	PCDD/F	dl-PCB
2019	TW-MOSS-DR-1901	30/09/2019	C	370	S	0.05	0.03	0.02
2020	20TWC-mos-01	29/11/2020	C	370	S	1.20	1.00	0.20
2021-1	20TWF-MOS-01DR	02-05-2021.	F=B	410	SSW	1.03	1	0.03
	20TWC-MOS-02DR	02-05-2021.	C1	385	S	1.13	1.1	0.03
2021-2	21-TWZ-MOS-06-C3	09/10/2021	C3	650	S	0.57	0.45	0.12
	21-TWZ-MOS-01-C	09/10/2021	C	370	S	0.48	0.41	0.07
	21-TWZ-MOS-04-C1	09/10/2021	C1	385	S	2.31	2.00	0.31
	22-TWZ-MOS-05-C1	09/10/2021	C1 (glas)	385	S	1.01	0.96	0.05
	22-TWZ-MOS-04-C1	09/10/2021	C1 (plastic)	385	S	0.68	0.59	0.09
2021-2	21-TWZ-MOS-CC1	09/10/2021	5 samples pooled			1.01	0.88	0.13

Average

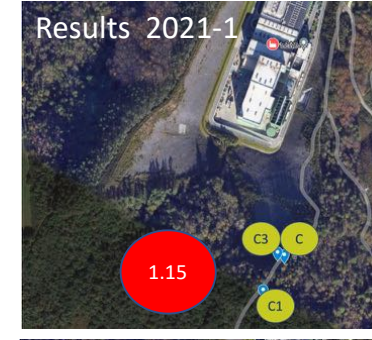
		DR CALUX pg TCDD eq/g product (MB)		
Year	Number	PCDD/F/dl-PCB	PCDD/F	dl-PCB
2019	n=1	0.05	0.03	0.02
2020	n=1	1.20	1.00	0.20
2021-1	n=2	1.08	1.05	0.03
2021-2	n=5	1.01	0.88	0.13

TW Indicative scale Results	
DR CALUX	
> 5.0 pg TCDD eq./g product	
> 2.0 pg TCDD eq./g product	
1.0 - 2.0 pg TCDD eq./g product	
0.5 - 1.0 pg TCDD eq./g product	
< 0.5 pg TCDD eq./g product	



pg TCDD eq./g product

Average				
DR CALUX pg TCDD eq/g product (MB)				
Year	Number	PCDD/F/dl-PCB	PCDD/F	dl-PCB
2019	n=1	0.05	0.03	0.02
2020	n=1	1.20	1.00	0.20
2021-1	n=2	1.08	1.05	0.03
2021-2	n=5	1.01	0.88	0.13





TWZ-MOSS-04

TW extra analyses on packaging
 Result:
 no influence of LDPE package material (plastic bag) of migration dioxin into these moss samples. These moss analysis results verifies the elevation of dioxin in mosses near the incinerator

TWZ-MOSS-05



Geo-location: 43.253150, -2.040300



Biomonitoring Mosses Zubieta 2019-2021														
Sample Date	Total	Samples	Location	Wind direction	Distance m	Year	TW-REF-NR number	Analysis	Upperbound (UB)					
									PCDD/F DR CALUX	dl-PCB DR CALUX	PCDD/F/dl-PCB DR CALUX	PFAS CALUX	PFAS FITC-T4	
									pg TCDD eq./g		µg PFOA eq./g	µg PFOA eq./g		
Veg. Moss: 2019														
30/09/2019	1	Moss	Loc. C (Gey)	South	370	2019	TW-MOS-DR-1901	DR CALUX	LOQ<0.06	LOQ<0.04	LOQ<0.1			
13/09/2019	2	Moss pooled	Near MWI/ Loc. B,	South	400-370	2019	TW-MOS-HM-1902	Heavy Metals*						
Veg. Moss: 2020														
29/11/2020	1	Moss	Loc. C	South	370	2020	20TWC-MOS-01	DR CALUX	1.0	0.2	1.2			
29/11/2020		Moss	Loc. C	South	370	2020	20TWC-MOS-01	PFAS CALUX				1.5		
02-05-2021.	2	Moss	F	South	406	2020	20TWF-MOS-01DR	DR CALUX	1.0	0.05	1.05			
			F=B				20TWB-MOS_01DR					5.0		
02-05-2021.	1	Moss	C' =Loc C1	South	355	2020	20TWC-MOS-02DR	DR CALUX	1.1	0.05	1.15			
02-05-2021.		Moss	C' =Loc C1	South	355	2020	20TWC-MOS-02PF	PFAS CALUX				3,9		
02-05-2021.		Moss	F	South	406	2020	20TWF-MOS-01PF	PFAS CALUX						
25-04-2021.	3	Moss	Zaldibia	South	26000	2020	20TWZ-MOS-03DR	DR CALUX	1.4	0,05	1.45			
25-04-2021.		Moss	Zaldibia		26000	2020	20TWZ-MOS-03PF	PFAS CALUX				2.8		
Veg. Moss: 2021														
09/10/2021	1	Moss	Loc. C	South	370	2021	21TWZ-MOS-01-C	DR CALUX	0.41	0.074	0.484			
09/10/2021	2	Moss	Loc. C1	South	355	2021	21TWZ-MOS-04-C1	DR CALUX	2.0	0.31	2.31			
					355	2021	21TWZ-MOS-04-C1	FITC-T4					17,0	
09/10/2021	3	Moss	Loc. C3	South	460	2021	21TWZ-MOS-06-C3	DR CALUX	0.45	0.12	0.57			
09/10/2021	4	Moss	Zaldibia	South	39000	2021	21TWZ-MOS-07-ZAL	DR CALUX	0.46	LOQ < 0.06	0.52			
						2021	21TWZ-MOS-07-ZAL	FITC-T4					4,2	
09/10/2021	5	Moss C1	Loc. C1	South	355	2021	21TWZ-MOS-05-C1	DR CALUX	0,96	0,05	1,01			
09/10/2021	6	Moss C1	Loc. C1	South	355	2021	21TWZ-MOS-04-C1	DR CALUX	0,59	0,09	0,68			

There are more than 8000 PFAS compounds and analysis is limited.

The analyse technique of FITC-T4 means fluorescent-labelled thyroxine (FITC-T4) consisting of fluorescein isothiocyanate (FITC) and L-thyroxine (T4).

PFAS CALUX is a very novel bio detection technique.

Both assays are expressed in µg PFOA equivalent/gram product.

PFAS in biomarkers															
Country	Date	Matrix		Distance	Date	Location	Ref. Nr.	PCDD/F/dl-PCB	PCDD/F	PCB	Dioxins/PCB	PAH	PFAS (FITC-T4)	PFAS CALUX	PFAS
				m				pg BEQ/g ds			ng BAP/g ds	µg PFOA eq/g	µg PFOA eq/g	theoretical	
EUS	2020	Sediment	1	471	2020	Zubieta	20-TW-SEDdn-01							0.063	0.49
EUS	2020	Sediment	2	187	2020	Zubieta	20-TW-SEDup-02							0.14	1.09
CZ	2021	Egg	2	4310	2021	Pilsen	TW-CZ21-Egg02	20.00	10.00	10.00	100%		1.2	0.25	1.2
CZ	2021	Egg	4	1750	2021	Pilsen	TW-CZ21-Egg04	3.30	1.30	2.00	65%		1.4	0.13	1.4
CZ	2021	Mosses	1	3400	2021	Pilsen	TW-CZ21-MOS-01	0.42	0.29	0.13	223%	12.00	1.6		1.6
CZ	2021	Mosses	3	420	2021	Pilsen	TW-CZ21-MOS-03.0/3.1/3.2	1.60	1.20	0.40	300%	13.00	1.7		1.7
EUS	2021	Egg	13	3700	2021	Zubieta	21TWZ-E03-13a	4.90	2.60	2.30	113%		1.9		1.9
EUS	2021	Egg	1p	1610	2021	Zubieta	21TWZ-E01-1p	1.90	0.94	0.96	98%		1.9		1.9
EUS	2021	Mosses	Zal2	39000	2021	Zubieta	21-TWZ-MOS-07-ZAL	0.52	0.46	0.03	1533%		4.2		4.2
LT	2021	Mosses	1	569	2021	Kaunas	TW21LT-Mos-01	3.37	2.80	0.57	491%	230.00	8.4		8.4
EUS	2020	Mosses	1	370	2020	Zubieta	20TWC-mos-01	1.20	1.00	0.20	500%			1.5	11.7
LT	2021	Mosses	3	465	2021	Kaunas	TW21LT-Mos-03	1.48	1.30	0.18	722%	210.00	13.0		13.0
ES	2021	Cupressus a.	13	400	2021	Madrid	TW-MD21-Veg-13/14/15	1.70	1.60	0.10	1600%	380.00	17.0		17.0
ES	2021	Cupressus a.	23	3820	2021	Madrid	TW-MD21-Veg-23	0.80	0.73	0.07	1043%	31.00	17.0		17.0
EUS	2021	Mosses	C1	400	2021	Zubieta	21TWZ-MOS-04-C1	2.31	2.00	0.31	645%		17.0		17.0
EUS	2020	Mosses	B	26000	2020	Zubieta	20TWZ-MOS-03DR	1.43	1.4	0.03	4667%			2.8	21.84
ES	2021	Pinus s.	20	3700	2021	Madrid	TW-MD21-Veg-20/22/23	0.14	0.08	0.06	133%	8.10	22.0		22.0
ES	2021	Pinus s.	1	570	2021	Madrid	TW-MD21-Veg-01/02	8.40	7.10	1.30	546%	220.00	26.0		26.0
EUS	2020	Mosses	C	385	2020	Zubieta	20TWC-MOS-02DR (C)	1.15	1.1	0.03	3667%			3.9	30.42
EUS	2020	Mosses	C1	410	2020	Zubieta	20TWB-MOS-01DR (C1)	1.05	1	0.03	3333%			5	39

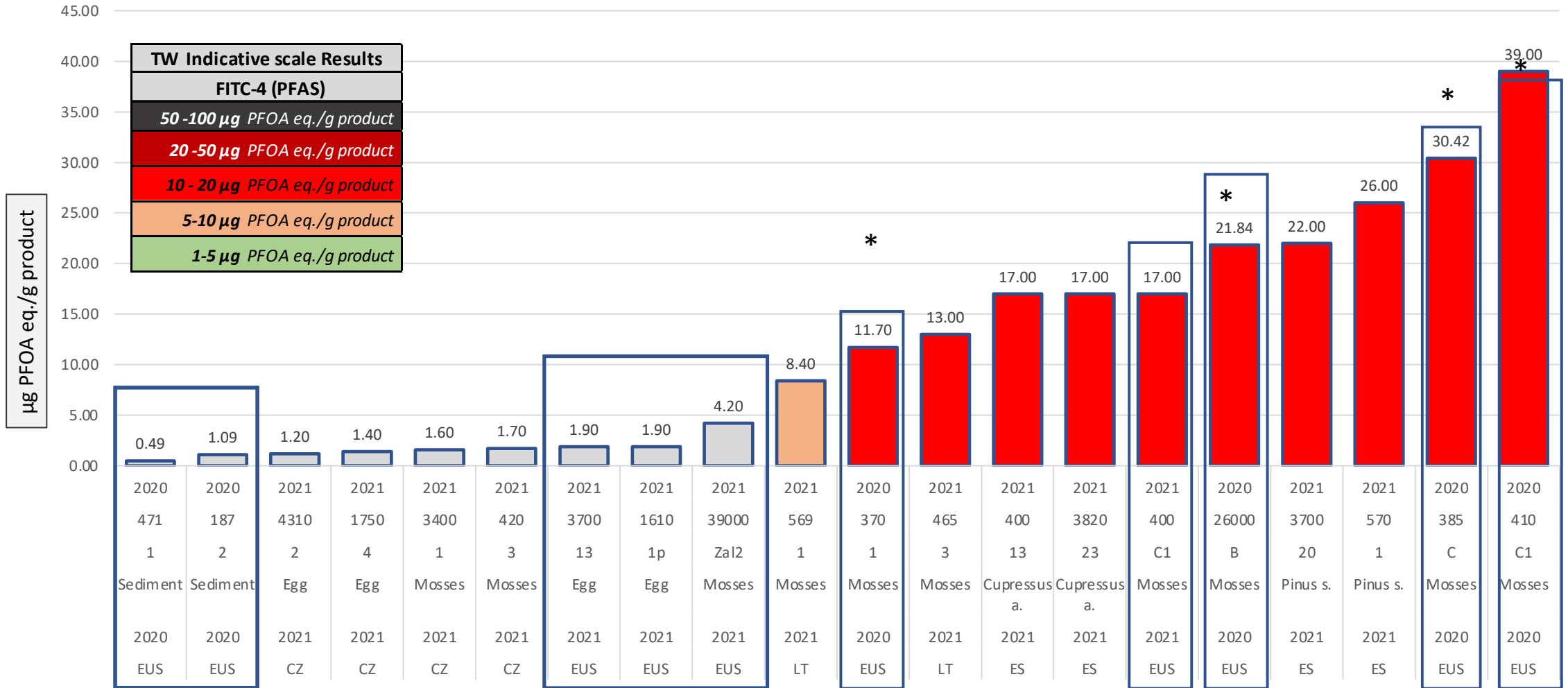
Blue:

PFAS Theoretical:

< LOD (Limit of Detection)

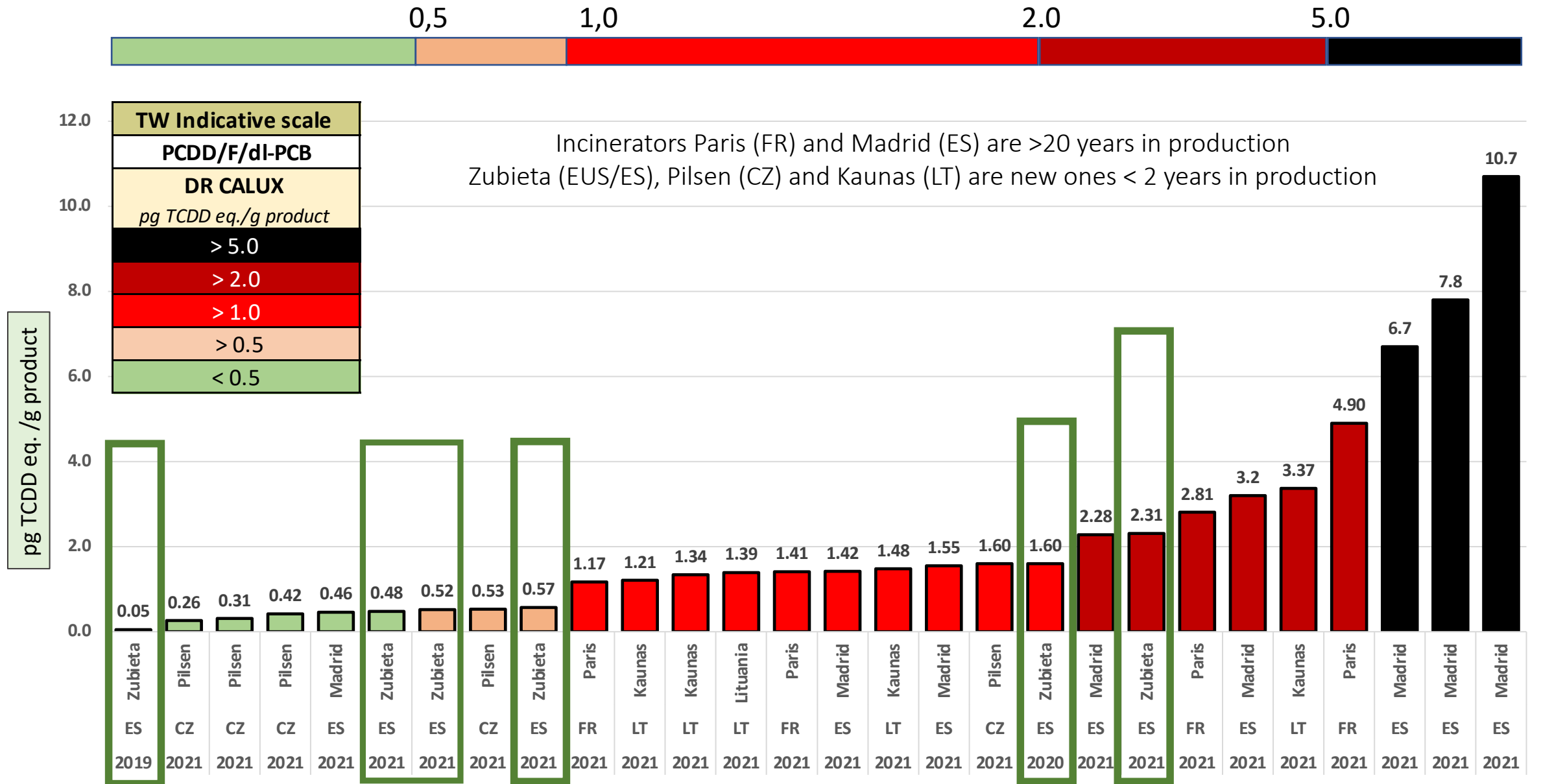
Calculation factor is used for PFAS CALUX to FITC-T4 with a factor 8.5.

This is based on two parallel analyses on eggs with PFAS CALUX and FITC-T4.

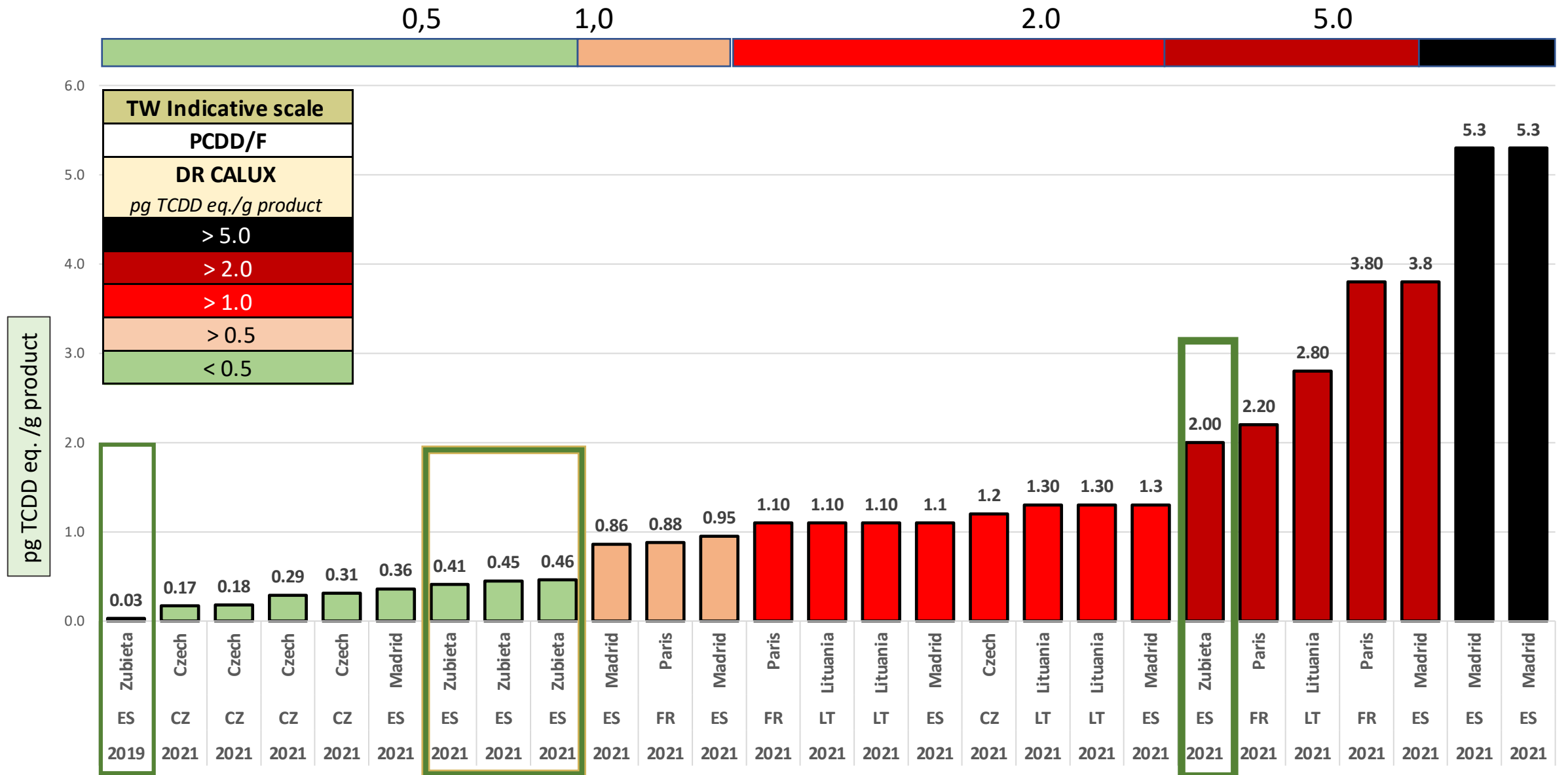


* Calculated FITC-T4 values of biomatrices analysed with PFAS CALUX

Indicative scale PCDD/F/dl-PCB in mosses Zubieta - 2021



Indicative scale PCDD/F in mosses Zubieta, Basque country 2021



Sediment 1
Results
ERaCALUX
PFAS

S1



Results 2020

ERaCALUX: **0.040** ng 17b Estradiol eq./g dw

PFAS: **0.063** µg PFOA eq./g dw

20TW-SEDDn-01
downstream WtE
ERaCALUX: **0.040**
PFAS: **0.063**

X: 577805.847
Y: 4790075.966

Results 2021

ERaCALUX: **LOQ < 0.0039** ng 17b Estradiol eq./g dw

Sampled in October, 2021



Sediment 2
Results
ERaCALUX
PFAS

S2



20TW-SEDup-02
upstream WtE
EraCALUX: **0.018**
PFAS: **0.014**

X: 577786.671
Y: 4789545.487

Results 2021

ERaCALUX: LOQ < 0.0051 ng 17b Estradiol eq./g dw
Samples in okt. 2021

Sediment 3
Results
ERaCALUX
PFAS

S3

20TW-SED-03
near biomass river
ERaCALUX: **LOQ<0.036**
PFAS: in preparation

X: 578570.687
Y: 4790055.041



Results 2020
ERaCALUX: **LOQ<0.036** ng 17b Estradiol
eq./g dw

No analyses in 2021



Sediment 4
Results
ERaCALUX
PFAS

S4

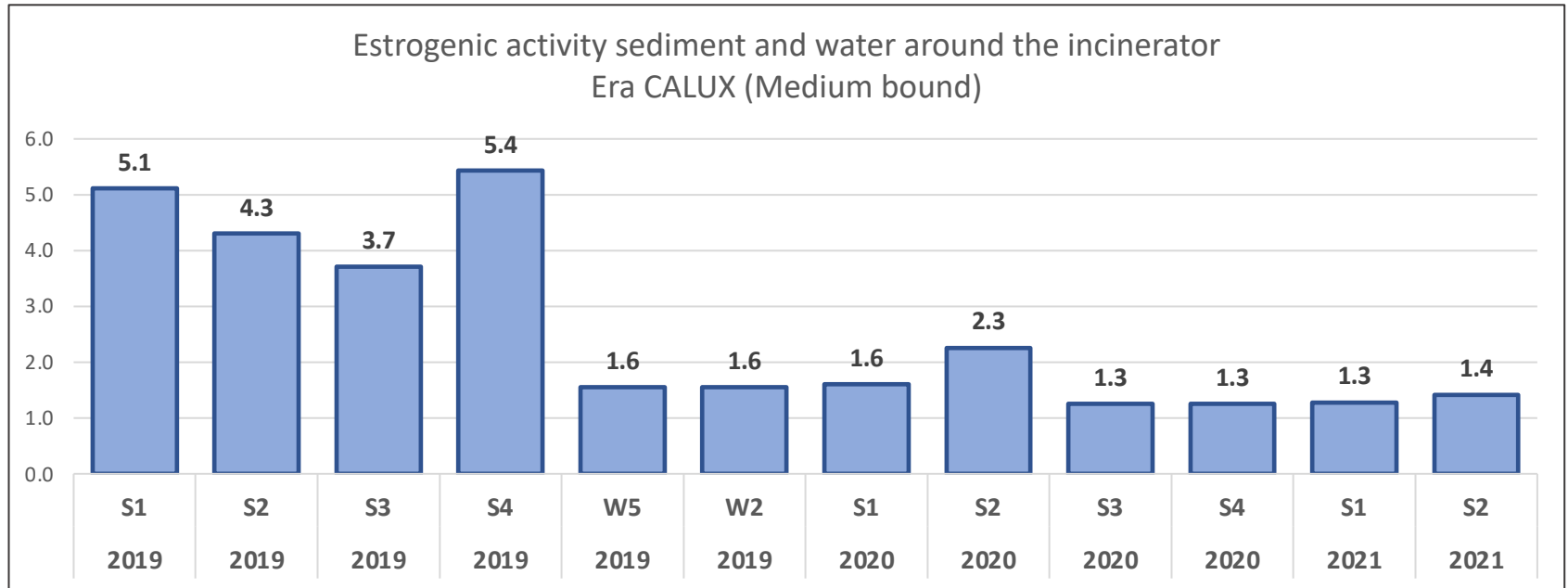
20TW-SED-04
See map location
ERaCALUX: **0.040**
PFAS: **0.063**

X: 578535.566
Y: 4788222.855



Sampled in 2021: not analysed

10 log fg 17b estradiol eq./g



Legenda	
S1	Location 1 - Arkaitzerreka - downstream WtE
S2	Location 2 - Arkaitzerreka stream- upstream V
S3	Location 3- near biomass river
S4	Location 4 - Abalotz stream
W2	Arkaitzerreka upstream WtE
W5	Gainaundi, underground water

Calamity 1: dead eels in stream



Calamity 2: Contaminated brown water



Initial results of the analysis



Id.Ciente:				52467
Id.Agrupación:	Id.Analito:	Unidades	Incertidumbre	MS4365-22-15639
Arsénico disuelto	48750	µg/l	31,7	6,76
Cadmio disuelto	48748	µg/l	19,3	< 2,5 (< 0,5)
Calcio	48717	mg/l	28,9	177
Cobre disuelto	48746	µg/l	28,1	5,59
Cromo disuelto	48736	µg/l	29	129
Hierro disuelto	48731	mg/l	33,6	5,58
Magnesio	48718	mg/l	26,1	30,1
Mercurio disuelto	48749	µg/l	32,2	< 1,0 (< 0,2)
Níquel disuelto	48733	µg/l	23,4	81
Plomo disuelto	48745	µg/l	29,6	3,95
Zinc disuelto	48747	µg/l	28,1	36
Cloruros	48682	mg/l	25,4	487
Fluoruros	48704	mg/l	25,7	0,247
Nitratos	48686	mg/l	26	1,2
Ortofosfatos	48826	mg PO4/l	26,2	< 0,75
Sulfatos	48681	mg/l	26,2	42,9
Amonio	48763	mg/l	25,7	117
Conductividad a 25 °C	48222	µS/cm	17,7	3610
pH	48221	unid. de pH	0,3	7,41
Tensioactivos aniónicos (SAAM)	48397	mg/l	28	0,271
Carbono Orgánico Total	5000521	mg/l	28	215
DBO5 Total	48290	mg/l	28	No Realizado
Demanda Química de Oxígeno (DQO)	5000124	mg/l	30,2	451
Sólidos en Suspensión	48169	mg/l	20,3	86
Turbidez	48398	unf	25	59,6

TW remarks on initial results, based on Dutch (NL) norms

Upper limit Calcium : 180 mg/l

Chromo: **129 µg/l**, norm: 50 µg/l

Nickel: **81 µg/l**, norm: 20 µg/l

Chlorine: **487 mg**,
drinkwater norm 0,25 mg/l,
basic water: 150 mg/l

Ammonium: **117 mg/l**,
Norm 0.608 mg/l

Conductivity: **3610 µS/cm**
Norm: 1.216 µS/cm

TOC: **215 mg/l**, norm 3 mg/l

Chemical oxygen demand: **451 mg/l**,
norm: 40 mg/l

Bijlage A: KRW-parameters

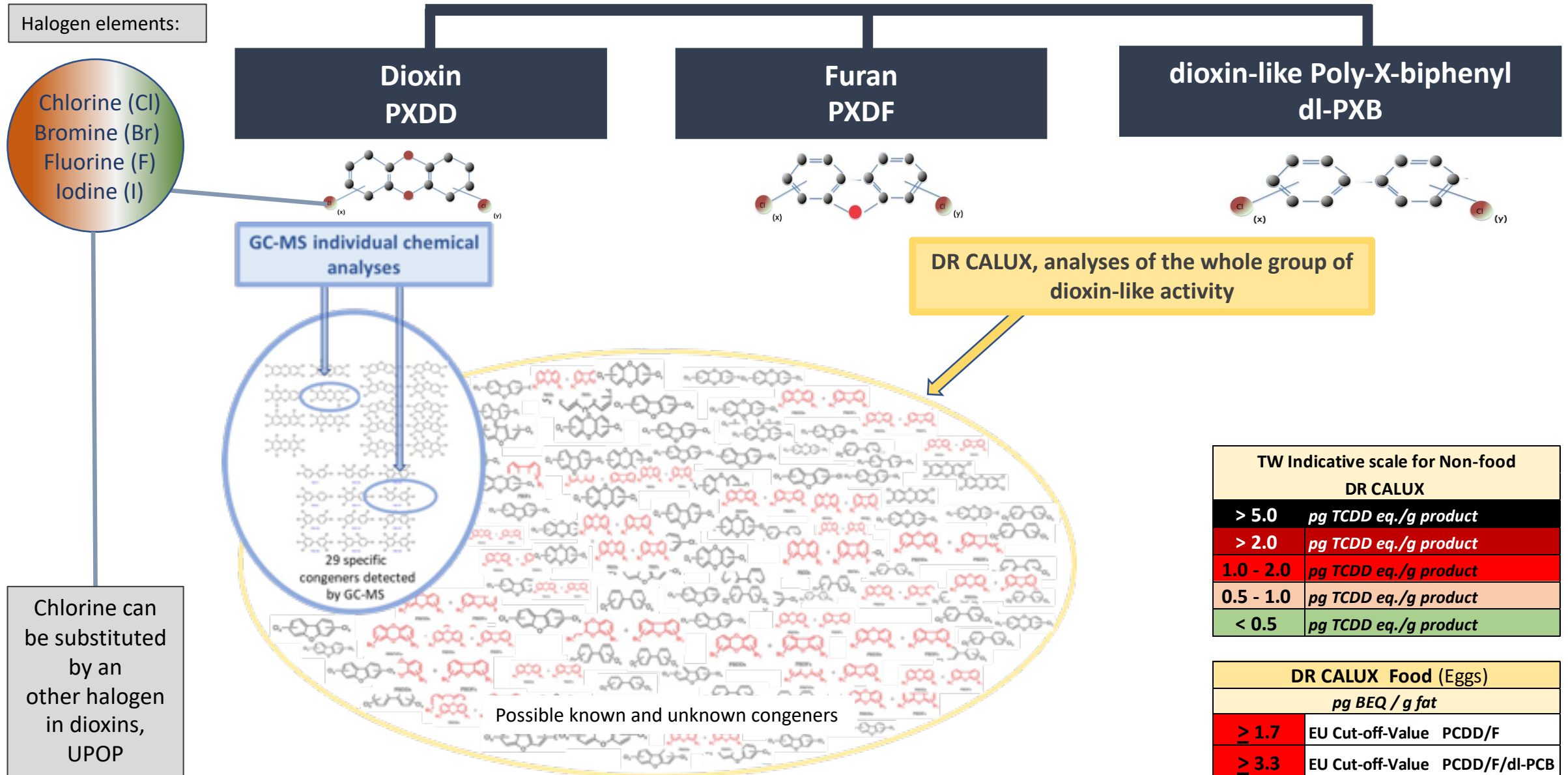
Parametercode	Naam
12DOC2a	1,2-dichloorethaan
12DOC3a	1,2-dichloorpropan
44DOT	4,4'-dichloordifenyldichloorethaan
4C9yFol	4-nonylfenol
4CIAn	4-chlooraniline
4tCBYfol	4-tertiair-octylfenol
abmctne	abamectine
acnfn	acnifen
Ag	zilver
aICI	alachloor
Ant	antraceen
As	arsen
atzme	atrazine
B	boor
Ba	barium
BaA	benzo(a)antraceen
BaP	benzo(a)pyreen
BbF	benzo(b)fluorantheen
Be	beryllium
Ben	benzeen
benzn	benzazon
bfnx	bifenox
BghiPe	benzo(ghi)peryleen
BIOLT	Biologie totaal
BkF	benzo(k)fluorantheen
C1yazfs	methylazinfos
C1ymafm	methyl-metsulfuron
C1yprmf	methylpirimifos
C1yprtn	methylparathion
C2yazfs	ethylazinfos
C2yBen	ethylbenzeen
C2yClprfs	ethylchloropyrifos
C2yprtn	ethylparathion
captn	captan
carbdam	carbendazim
Cd	cadmium
CHEMT	Chemische toestand
Chr	chryseen
Cl	chloride
Clvfs	chlorfeninfos
Clidzn	chloridazon
Clpfn	chlorprofam
Cltn	chlorotoluron
Co	kobalt
Cr	chrom
Cu	koper
cypmtn	cypmethrin
Dazn	diazinon
DC4ySn	dibutyltin (kation)
Dcfl	dicofol

Parametercode	Naam
DCIC1a	dichloormethaan
DCIppP	dichloorprop-P
DCIvs	dichloorvos
DEHP	bis(2-ethylhexyl)ftalaat (DEHP)
Dmtat	dimethoaat
dmtn	deltamethrin
DmtnmCP	dimethenamid-P
Durn	diuron
ECOLT	Ecologie toestand of potentieel
endsh	endosulfan (som alfa- en beta-isomeer)
esfvrt	esfenvaleraat
Fen	fenantreen
fenamfs	fenamifos
fenOZtan	fenitrothion
fenOxnb	fenoxycarb
fenton	fenthion
Flu	fluorantheen
FYSOHEM	Algemene fysisch-chemische parameters
FYTOL	Fytoplankton-kwaliteit
HCb	hexachloorbenzeen
heptnfs	heptenofos
Hg	kwik
HxCltDen	hexachloorbutadien
imdcpd	imidacloprid
ipm	isoproturon
ingrl	irgarol
lyhltm	lambda-cyhalothrin
linn	linuron
MAFAUNA	Macrofauna-kwaliteit
malton	malathion
MCPA	2-methyl-4-chloorfenoxycarboxyzuur
MCPP	meconop
metbtazm	metabenthiazuron
metCl	metolachloor
mevfs	mevinfos
Mnrm	monolinuron
Mo	molybdeen
moCl	metazachloor
Naf	naftaleen
Nanorg	stikstof anorganisch
NH4	ammonium
Ni	nikkel
Ntot	stikstof totaal
NUTRIENT	Nutriënten
O2	zuurstof
omtat	omethoaat
OVWFLORA	Overige waterflora-kwaliteit
OWEINDOD	Eendoordeel oppervlaktewater
Pb	lood
PeClBen	pentachloorbenzeen
PeClFol	pentachloorfenol
PFOS	perfluorocctaansulfonaat
pH	Zuurgraad
pirnmb	pirimicarb
propox	propoxur
Ptot	fosfor totaal
pyrdbn	pyridaben
pyrpxfn	pyrproxifen
quinoxn	quinoxalen
s4C9yFol	som 4-nonylfenol-isomeren (vertakt)

Parametercode	Naam
Sb	antimoon
sC10C13Clakn	som C10-C13-chlooralkanen
sDOX4	som 2,4'-DDT, 4,4'-DDT, 4,4'-DDD en 4,4'-DDE
sdrin4	som aldrin, dieldrin, endrin en isodrin
Se	seleen
shCH4	som a-, b-, c- en d-HCH
shpCl2	som heptachloor en cis- en trans-heptachloorepoxide
simzine	simazine
Sn	tin
sPBDE6	som PBDE28, 47, 99, 100, 153, 154
STOFOV	Specifieke verontreinigende stoffen
STOFR_34-45	Prioritaire stoffen - nieuw vanaf 2013 - nr. 34 t/m 45
STOFR_UBQJ	Prioritaire stoffen - ubiquitair
STOFR_UBQN	Prioritaire stoffen - niet-ubiquitair
xyln	som xyleen-isomeren
T	Temperatuur
T4Cl2a	tetrachloormethaan (tetra)
T4Cl2e	tetrachlooretheen (per)
Tazfs	triazofos
TC4yPO4	tributylfosfaat
TC4ySn	tributyltin (kation)
TClBen	trichloorbenzeen
TClC1a	trichloormethaan (chloroform)
TClC2e	trichlooretheen (tri)
Te	Golfenergie in het spectrale domein
tefbzm	teflubenzuron
terbtm	terbutrin
terCl4yazme	terbutylazine
Tfrine	trifuraline
TfySn	trifenyln (kation)
Ti	titaan
Tl	thallium
tolchCl2y	tolclofos-methyl
U	uranium
V	vanadium
VIS	Vis-kwaliteit
ZICHT	Doorzicht
Zn	zink

Official governmental Water parameters for analyses water The Netherlands (NL)

More research is needed



Halogen elements:

- Chlorine (Cl)
- Bromine (Br)
- Fluorine (F)
- Iodine (I)

Chlorine can be substituted by another halogen in dioxins, UPOP

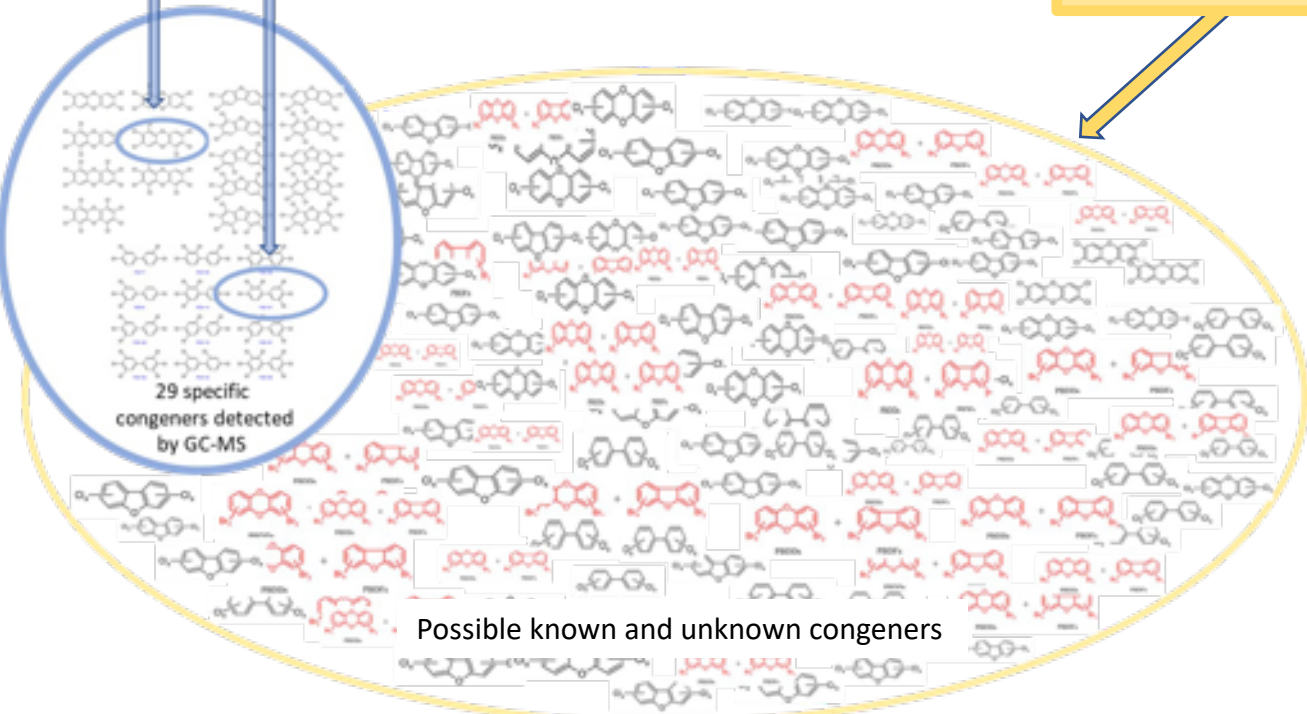
**Dioxin
PXDD**

**Furan
PXDF**

**dioxin-like Poly-X-biphenyl
dl-PXB**

GC-MS individual chemical analyses

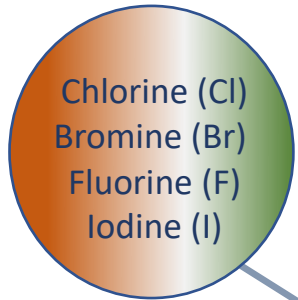
DR CALUX, analyses of the whole group of dioxin-like activity



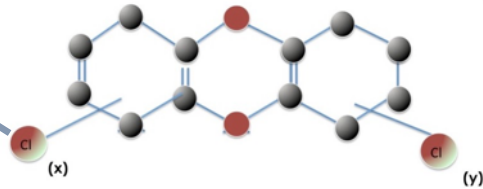
TW Indicative scale for Non-food DR CALUX	
> 5.0	pg TCDD eq./g product
> 2.0	pg TCDD eq./g product
1.0 - 2.0	pg TCDD eq./g product
0.5 - 1.0	pg TCDD eq./g product
< 0.5	pg TCDD eq./g product

DR CALUX Food (Eggs)	
pg BEQ / g fat	
> 1.7	EU Cut-off-Value PCDD/F
> 3.3	EU Cut-off-Value PCDD/F/dl-PCB

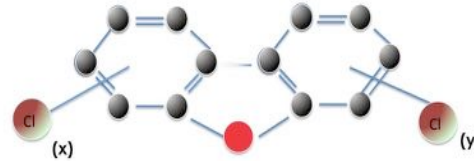
Halogen elements:



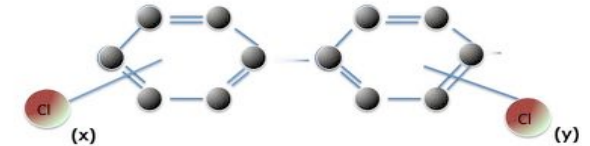
Dioxin
PCDD (75)
n = 7



Furan
PCDF (135)
n = 10



dioxin-like Polychlorobiphenyl
dl-PCB (209)
n = 12



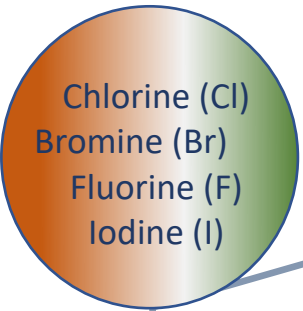
Congeners of chlorinated compounds (chemical GC-MS analysis)

Dioxins, furans (PCDD/F) and dioxin-like PCBs		
Abbreviation	Congeners	TEF
Dioxins (n=7)		
TCDD	2,3,7,8-Tetrachlorodibenzo-p-dioxin	1
PCDD	1,2,3,7,8-Pentachlorodibenzo-p-dioxin	1
HxCDD1	1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	0,1
HxCDD2	1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin	0,1
HxCDD3	1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin	0,1
HpCDD	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	0,01
OCDD	Octachlorodibenzo-p-dioxin	0,0003

Furans (n=10)		
TCDF	2,3,7,8-Tetrachlorodibenzofuran	0,1
PCDF1	1,2,3,7,8-Pentachlorodibenzofuran	0,03
PCDF2	2,3,4,7,8-Pentachlorodibenzofuran	0,3
HxCDF1	1,2,3,4,7,8-Hexachlorodibenzofuran	0,1
HxCDF2	1,2,3,6,7,8-Hexachlorodibenzofuran	0,1
HxCDF3	1,2,3,7,8,9-Hexachlorodibenzofuran	0,1
HxCDF4	2,3,4,6,7,8-Hexachlorodibenzofuran	0,1
HPCDF1	1,2,3,4,6,7,8-Heptachlorodibenzofuran	0,01
HPCDF2	1,2,3,4,7,8,9-Heptachlorodibenzofuran	0,01
OCDF	Octachlorodibenzofuran	0,0003

Polychlorinated biphenyl (n=12)		
PCB77	3,3',4,4'-Tetrachlorobiphenyl (#77)	0,0001
PCB81	3,4,4',5-Tetrachlorobiphenyl (#81)	0,0003
PCB126	3,3',4,4',5-Pentachlorobiphenyl (#126)	0,1
PCB169	3,3',4,4',5,5'-Hexachlorobiphenyl (#169)	0,03
PCB105	2,3,3',4,4'-Pentachlorobiphenyl (#105)	0,00003
PCB114	2,3,4,4',5-Pentachlorobiphenyl (#114)	0,00003
PCB118	2,3',4,4',5-Pentachlorobiphenyl (#118)	0,00003
PCB123	2,3,4,4',5-Pentachlorobiphenyl (#123)	0,00003
PCB156	2,3,3',4,4',5-Hexachlorobiphenyl (#156)	0,00003
PCB157	2,3,3',4,4',5'-Hexachlorobiphenyl (#157)	0,00003
PCB167	2,3',4,4',5,5'-Hexachlorobiphenyl (#167)	0,00003
PCB189	2,3,3',4,4',5,5'-Heptachlorobiphenyl (#189)	0,00003

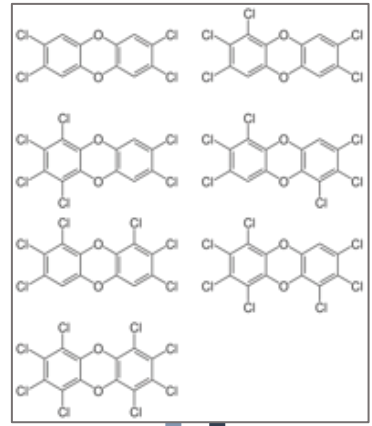
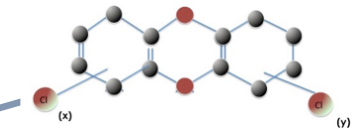
Halogen elements:



Chlorine can be substituted by an other halogen in dioxins, UPOP

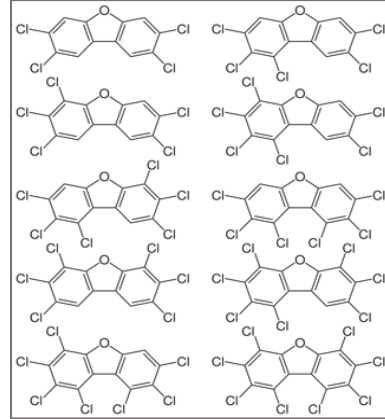
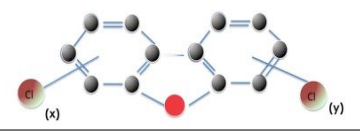
EU Regulated only the chlorinated sum of dioxins (PCDD/F/dl-PCB) for food and only dioxins (PCDD/F) in emissions

Dioxin PCDD (75) n = 7



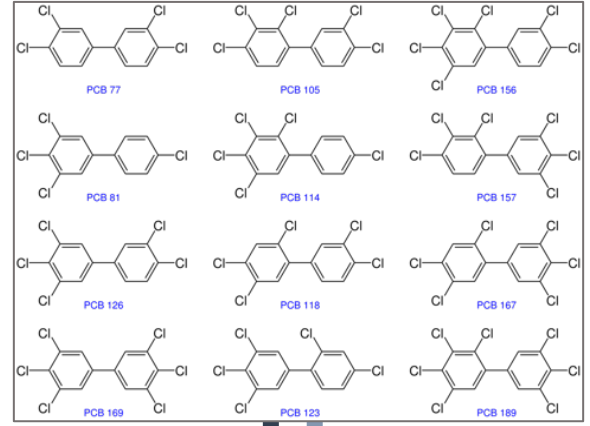
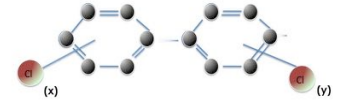
0.1 ng TEQ/Nm³

Furan PCDF (135) n = 10



0.1 ng TEQ/Nm³

dioxin-like Polychlorobiphenyl dl-PCB (209) n = 12



Food (Eggs)	GC-MS	pg TEQ/g fat
Non-food	GC-MS	pgTEQ/g product
≥ 5.0	EU Limit PCDD/F/dl-PCB	

Food (Eggs)	GC-MS	pg TEQ/g fat
Non-food	GC-MS	pgTEQ/g product
≥ 2.5	EU Limit PCDD/F	
≥ 1.75	EU Action level PCDD/F	

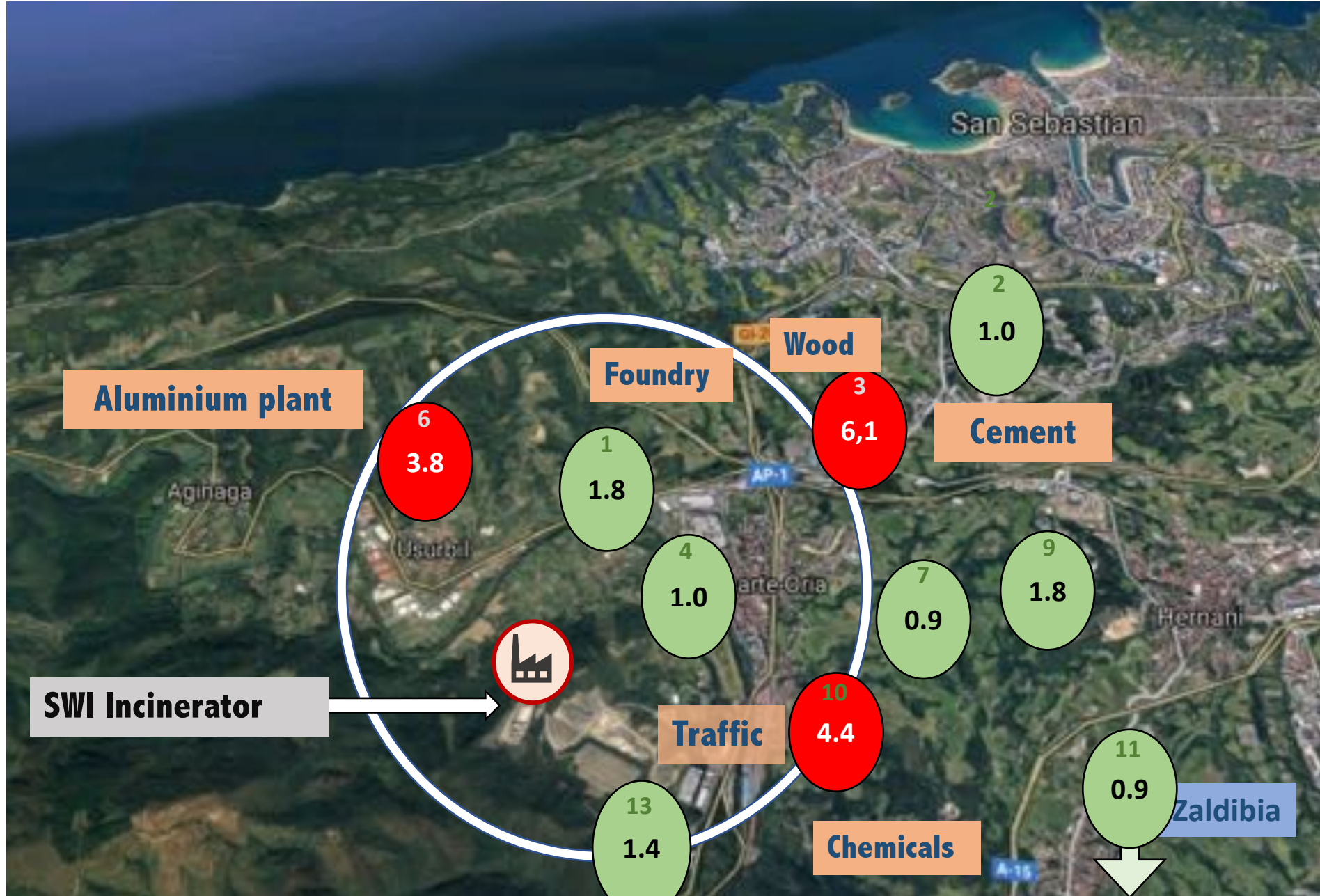
Food (Eggs)	GC-MS	pg TEQ/g fat
Non-food	GC-MS	pgTEQ/g product
≥ 2.5	EU Limit PCDD/F	
≥ 1.75	EU Action level PCDD/F	

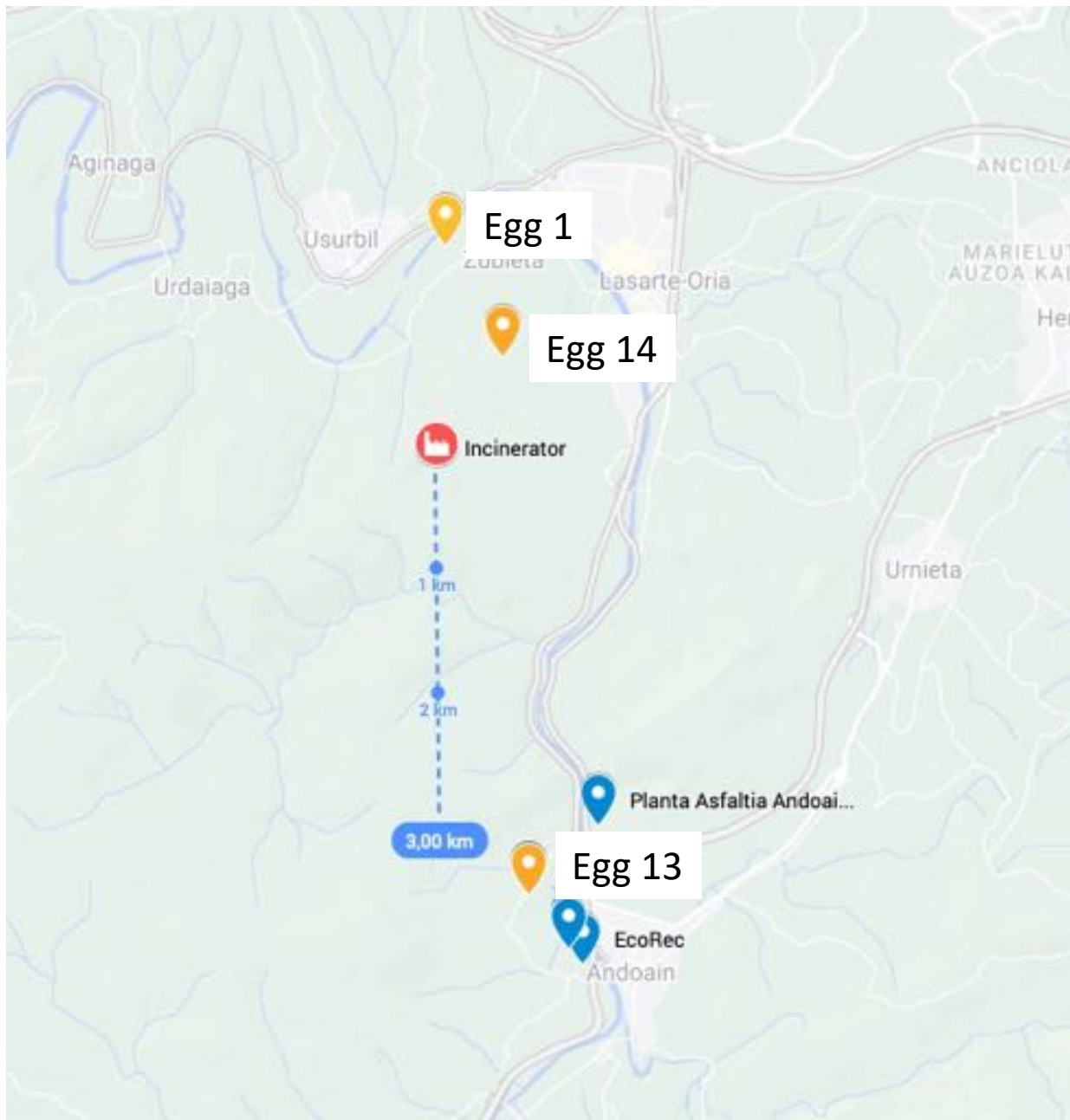
Food (Eggs)	GC-MS	pg TEQ/g fat
Non-food	GC-MS	pgTEQ/g product
≥ 1.75	EU Action level dl-PCB	

Eggs of backyard chicken, Zubieta 2021

Eggs 2021																			
1	V	1-10-2021	1	Location 1 Zubieta	"Press"	North	1610	2021	21TWZ-E01-1p	41611	Food egg	DR CALUX	0.94	0.96	1.9				
1	V	1-10-2021	1	Location 1 Zubieta	"Press"	North	1610	2021	21TWZ-E01-1p	41611	Food egg	FTIC-T4							1,9
2	V	1-10-2021	2	Location 13A - Intxusaran		South	3500	2021	21TWZ-E03-13A	41612	Food egg	DR CALUX	2.6	2.3	4.9				
	V	4-11-2021		Location 13A - Intxusaran		South	3500	2021	21TWZ-E03-13A	41730	Food egg	GC-MS				1.5	3.5	5.0	
	V	4-11-2021		Location 13A - Intxusaran		South	3500	2021	21TWZ-E03-13A	41730	Food egg	FTIC-T4							1,9
3	V	1-10-2021	3	Loaction 14p - Petritza		North	1370	2021	21TWZ-E02-14p	41613	Food egg	DR CALUX	0.81	0.59	1.4				

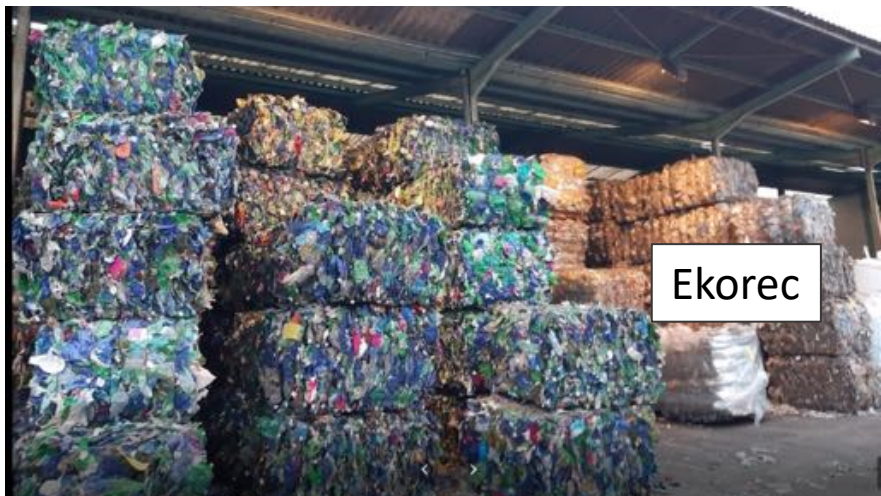






Zubieta, 2021			
Sample egg location questionnaire Zubieta, Spain - 2021			
TW-REF-NR	TWZ-01	TWZ-13	TWZ-14
Distance (m)	1650	3430	900
Winddirection	N	SSE	NNE
Pics permissions	yes	yes	yes
Breed	unknown	unknown	unknown
N hens	18	20	6
N rooster	1	1	0
Age (month)	12 till 60	18	11
Eggs/day	13 (CALC)	14 (calc)	5 (calc)
Eggs/week	88 (calc)	100 (calc)	35 (calc)
Eggs/month	378 (calc)	420 (calc)	150 (calc)
Foraging area	30	300	300
Housing	4	5	3
Terrain	soil, grass	soil, grass	soil, grass, stones
Feed	Left-over kitchen, garden	biological	left-over
	commercial ecological		commercial ecological
Outdoor fireplace	No		No
Housing material	Wood		Wood
All purpose burner	no		No
Pesticides use	no		No
DR CALUX pg BEQ /g fat			
PCDD/F	0.94	2.60	0.81
dl-PCB	0.96	2.30	0.59
PCDD/F/dl-PCB	1.90	4.90	1.4

Questionnaire



Ekorec

Circular economy

EKOREC, located in Andoain (Basque Country) is a reference in plastic's circular economy within Spain, especially in PET materials. We recycle PET bottles using post-consumer and post-industrial waste. The resulting flakes (color and transparent) are transformed into PET granule, agglomerate and PET sheet. Our customers (food&bev, pharma, home personal care, industry) use those materials to produce new packagings such as PET trays and bottles. In our production process we use sustainable materials and energy from our own Cogeneration Power Plant.



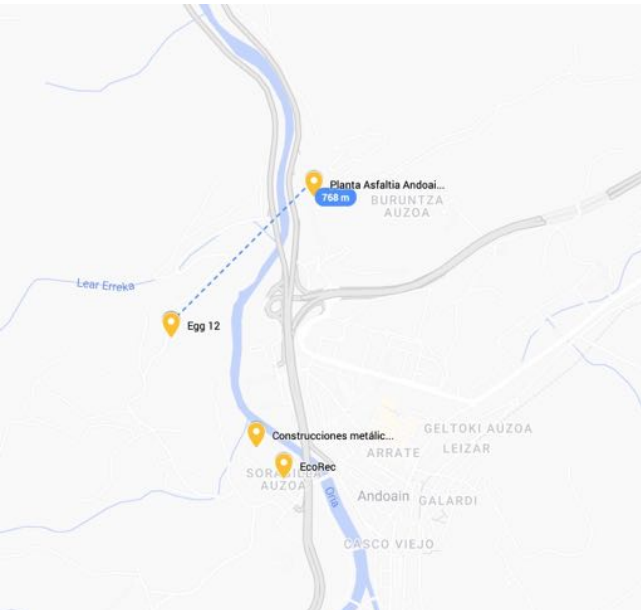
Metal construction

Construcciones metálicas Zazpi S.A.
Polígono, Borda Berri Kalea, 18, 2014 0 Andoain, Gipuzkoa



CERTIFICADO ZERO WASTE

Certificated zero waste



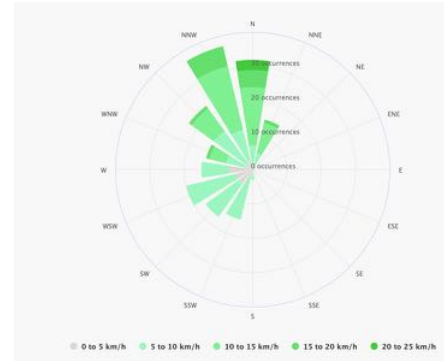
Egg location 1, 1610 m north from the incinerator

		DR CALUX			GC-MS		
		PCDD/F/dl-PCB	PCDD/F	dl-PCB	PCDD/F/dl-PCB	PCDD/F	dl-PCB
01/09/2019	19-TWZ-001	2.40	1.80	0.60			
27/01/2020	19-TWZ-001				3.11	1.17	1.94
01/09/2020	20TWZ-001	1.60	0.84	0.76			
01/10/2021	21TWZ-E01-1p	1.90	0.94	0.96			
	Cut-off	3.3	1.7		5	1.75	1.75

In 2020 a exceeding of the action limit of PCDD/F in the CALUX.
The verification show an exceeding of the action limit for dl-PCB.

In 2021 the values comply the EU-norm.

FITC-T4 PFAS: 1.9 µg PFOA eq/g fat



Egg location 1



Egg location 13, 3600 m south from the incinerator

		DR CALUX			GC-MS		
		PCDD/F/dl-PCB	PCDD/F	dl-PCB	PCDD/F/dl-PCB	PCDD/F	dl-PCB
01/09/2019	TWZ-013	1.40	1.40	0.00			
01/10/2021	21TWZ-E03-13a	4.90	2.60	2.30			
01/10/2021	21TWZ-E03-13a				5.00	1.50	3.50
	Cut-off	3.3	1.7		5	1.75	1.75

DR CALUX PCDD/F/dl/PCBIs suspect

GC-MS : PCDD/F/dl-PCb doesn't comply with EU limit of dioxins in food

GC-MS : dl-PCB exceed action limit

FITC-T4 PFAS: 1.9 µg PFOA eq/g fat



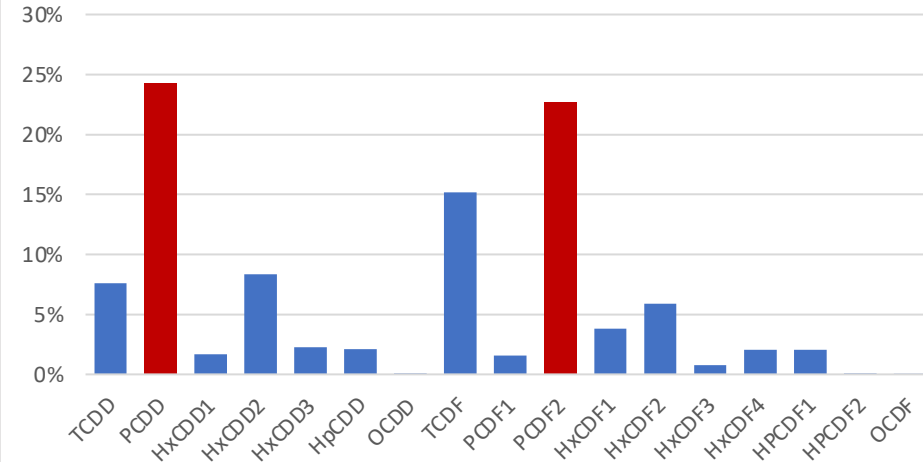
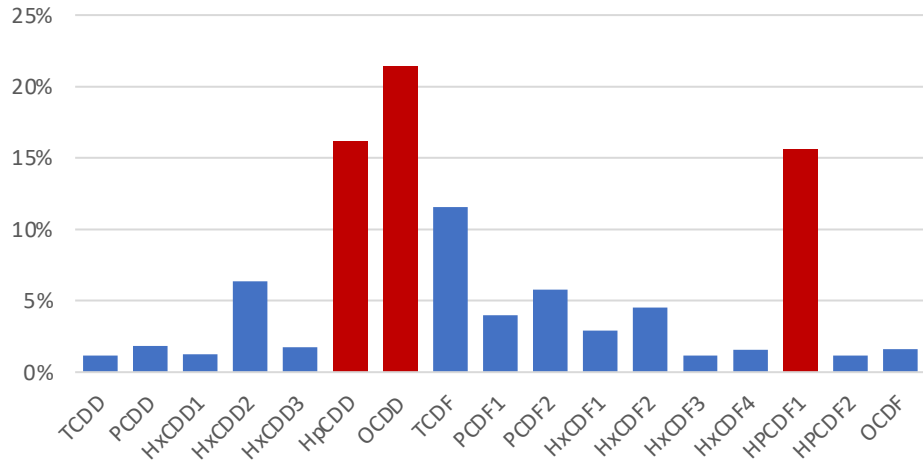
Egg location 13A

Fraction of total (%)

Fraction of total TEQ (%)

Concentration fingerprint location 13 (MB)

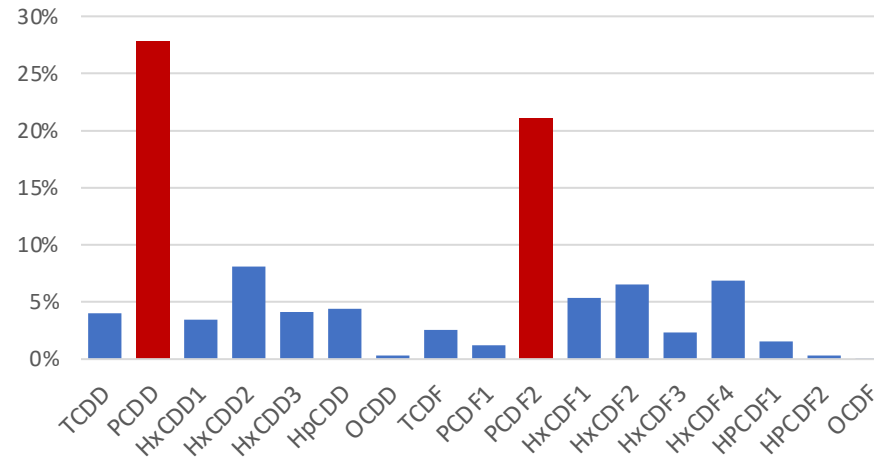
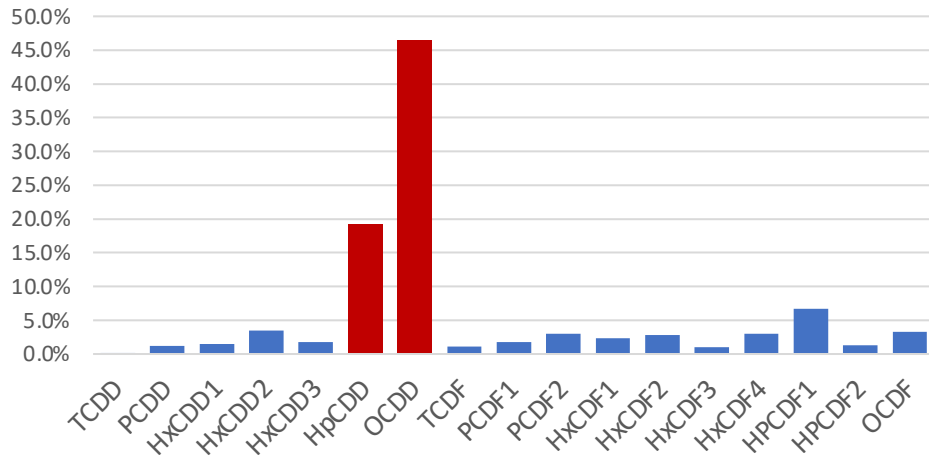
Fingerprint TEQ % PCDD/F (MB)



Fraction of total (%)

Incinerator REC/NL (20,000 hrs)

Fraction of total TEQ (%)



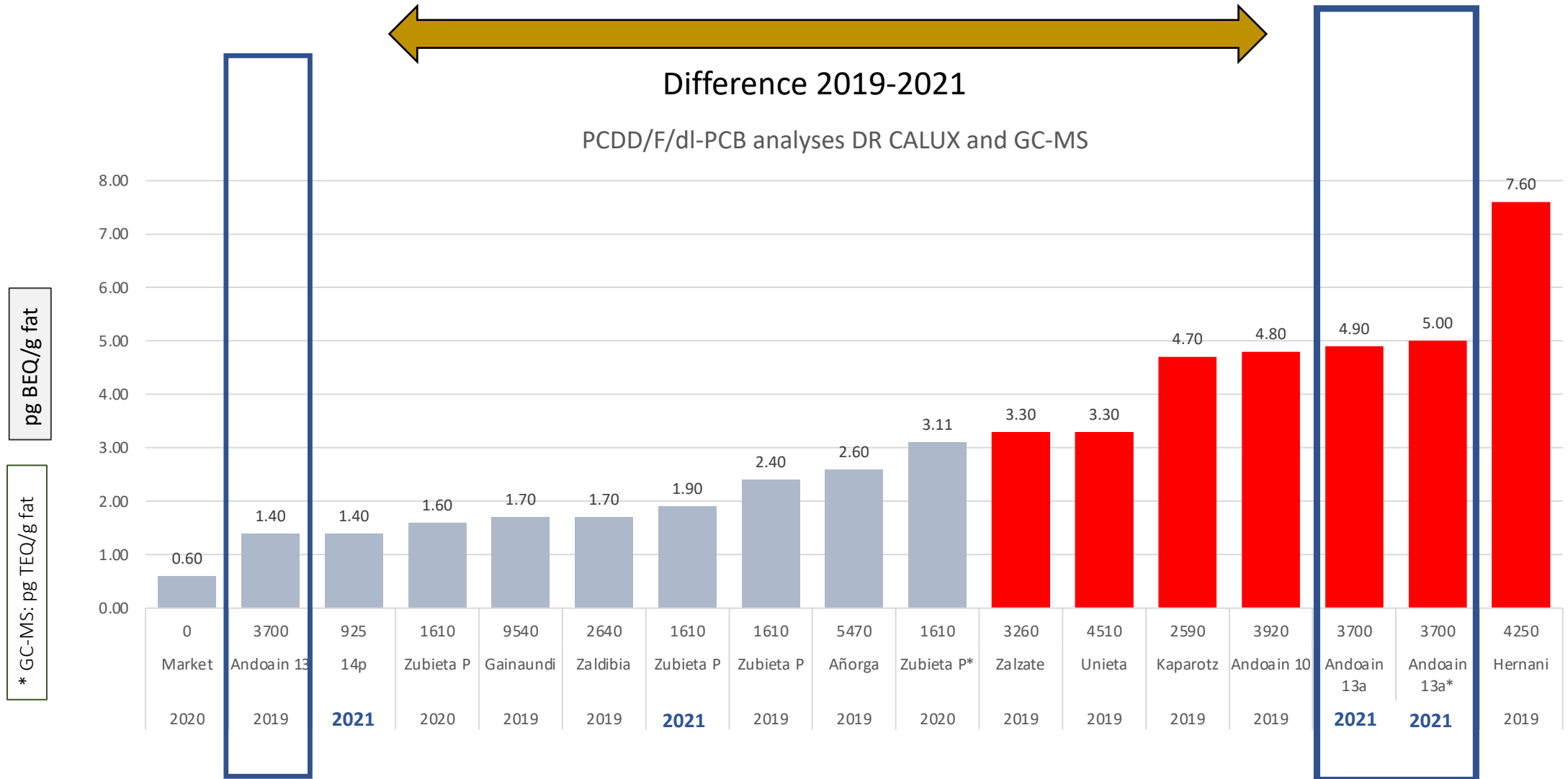
Need for fingerprint emission incinerator Zubieta

Egg location 14, 1370 m north from the incinerator - 2021

		DR CALUX			GC-MS		
		PCDD/F/dl-PCB	PCDD/F	dl-PCB	PCDD/F/dl-PCB	PCDD/F	dl-PCB
01/10/2021	21TWZ-E02-14p	1.4	0.81	0.59			
	Cut-off	3.3	1.7		5	1.75	1.75

Calux analysis complies with EU limit of dioxins in food/eggs





Key findings biomonitoring Zubieta 2021

- High dioxin levels in mosses near the incinerator
- Elevated dioxins at egg location (3600 m) in the main wind direction south of the incinerator
- Typical combustion congeners, like OCDD and HpCDF1, are found in the eggs
- PFAS found in the biomatrices mosses, eggs and sediment
- More research is needed in water stream near incinerator, because of calamities

Advice biomonitoring Zubieta 2022

- **Moss** sampling/analyses **dioxins in a circle all around incinerator** like in 2019.
- **Moss** sampling/analyses **PFAS** in a circle all around incinerator
- Analysis of ***Pinus radiata*** on **dioxins** and **PFAS**
- **Locations of backyard chicken** coops needs to **> 5**
- **Water spills need to be studied in relation with priority substances, like dioxins, PFAS**
- Mother **milk** research , repeat of 2019
- Exclude reference location moss from this research 2021
- Need for emissions patterns (congers)incinerator with long term sampling

Annex: sample and analyses

Biomonitoring Zubieta 2019-2021												Results 2019-2021							
Sample Date	Total	Samples	Location	Wind direction	Distance m	Year	TW-REF-NR number	BDS nr	Matrix BDS	Analysis	PCDD/F DR CALUX	dl-PCB DR CALUX	Upperbound (UB) PCDD/F/dl-PCB DR CALUX	PCDD/F GC-MS-ub	dl-PCB GC-MS	Upperbound (UB) PCDD/F/dl-PCB GC-MS	ERaCALUX	PFAS CALUX	PFAS FITC-T4
											1.7		3.3	2.5		5.0		µg PFOA	µg PFOA
											pg BEQ (TCDD)/g fat (veg: product)			pg TEQ/g fat (veg: product)			pg / 17b	dry weight	dry weight
																	µg PFOA eq./g	µg PFOA eq./g product	
Human Mother Milk 2019																			
1	1	1	V	oct.-2019	1	MM pooled	Lasarte	North-east	2046	2019	TW-MML-1901	36668	H. milk	DR CALUX	0.057	0.039	0.096		
2	2	2	V	oct.-2019	2	MM pooled	Usurbil	North-West	1500	2019	TW-MMU-1902	36667	H. milk	DR CALUX	0.074	0.106	0.180		
3	3	3	V	oct.-2019	3	MM pooled	Andoain	South-East	4150	2019	TW-MMA-1903	36669	H. milk	DR CALUX	0.095	0.065	0.160		
Veg. Moss: 2019																			
4	4	1	V	30-9-2019	1	Moss	Loc. C (Gey)	South	370	2019	TW-MOS-DR-1901	36670	Food /veg.	DR CALUX	LOQ<0.06	LOQ<0.04	LOQ<0.1		
5	5		V	13-9-2019	2	Moss pooled B, C	Near MWI / Loc. B, C	South	400-370	2019	TW-MOS-HM-1902			Heavy Metals*					
Veg. Moss: 2020																			
6	1	1	V	29-11-2020	1	Moss	Loc. C	South	370	2020	20TWC-MOS-01	39356	not defined	DR CALUX	1.0	0.2	1.2		
7	2		V	29-11-2020		Moss	Loc. C	South	370	2020	20TWC-MOS-01	39356	not defined	PFAS CALUX					1.5
8	3	2	V	02-05-2021	2	Moss	F	South	406	2020	20TWF-MOS-01DR	40625	not defined	DR CALUX	1.0	0.05	1.05		
9	4	3	V	02-05-2021	1	Moss	F=B	South	355	2020	20TWF-MOS-01DR								5.0
19	5		V	02-05-2021		Moss	C' =Loc C1	South	355	2020	20TWC-MOS-02DR	40624	not defined	DR CALUX	1.1	0.05	1.15		
							C' =Loc C1	South	355	2020	20TWC-MOS-02PF	40627	not defined	PFAS CALUX					3,9
11	6		V	02-05-2021		Moss	F	South	406	2020	20TWF-MOS-01PF	40628	not defined	PFAS CALUX					
12	7	4	V	25-04-2021	3	Moss	Zaldibia	South	26000	2020	20TWZ-MOS-03DR	40626	not defined	DR CALUX	1.4	0,05	1.45		
13	8		V	25-04-2021		Moss	Zaldibia	South	26000	2020	20TWZ-MOS-03PF	40629	not defined	PFAS CALUX					2.8
Veg. Moss: 2021																			
14	1	1	V	9-10-2021	1	Moss	Loc. C	South	370	2021	21TWZ-MOS-01-C	41614	not defined	DR CALUX	0.41	0.074	0.484		
15	2	2	V	9-10-2021	2	Moss	Loc. C1	South	355	2021	21TWZ-MOS-04-C1	41615	not defined	DR CALUX	2.0	0.31	2.31	pooled	
16	3								355	2021	21TWZ-MOS-04-C1	41615	not defined	FITC-T4					17,0
									355	2021	21TWZ-MOS-05-C1			DR CALUX					
17	4	3	V	9-10-2021	3	Moss	Loc. C3	South	460	2021	21TWZ-MOS-06-C3	41617	not defined	DR CALUX	0.45	0.12	0.57		
18	5	4	V	9-10-2021	4	Moss	Zaldibia	South	26000	2021	21TWZ-MOS-07-ZAL	41616	not defined	DR CALUX	0.46	LOQ < 0.06	0.52		
19	6									2021	21TWZ-MOS-07-ZAL	41616	not defined	FITC-T4					4.2
20	7	5	V	9-10-2021	5	Moss C1	Extra analyse 17-06-2022	South	355	2021	21TWZ-MOS-05-C1	43131	not defined	DR CALUX	0,96	0,05	1,01	pooled	
21	8	6	V	9-10-2021	6	Moss C1	Extra analyse 17-06-2022	South	355	2021	21TWZ-MOS-04-C1	43132	not defined	DR CALUX	0,59	0,09	0,68	pooled	



Samples in 2019, in Total: **26 analysis** MM-3, Mosses-2, Veg-4, Sediment-4, Water-2, Eggs-10 locations / 11 analysis



Samples in 2020, in Total: **18 analysis** MM-0, Mosses-8, Veg-2, Sediment-6, Water-0, Eggs-2 locations / 2 analysis



Samples in 2021, in Total: **16 analysis** MM-0, Mosses-8, Veg-0, Sediment-2, Water-0, Eggs-3 locations / 6 analysis

2019- 2021 = Total: 60 analysis

