Hormones and Antibiotics in Solids

presented by

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Exploring the problematic: context

presence of pharmaceuticals and steroid hormo
environment are a product of human (as well as a
umption and release though feces and urine.

Incomplete treatment in wastewater plants

Introduction into the environm

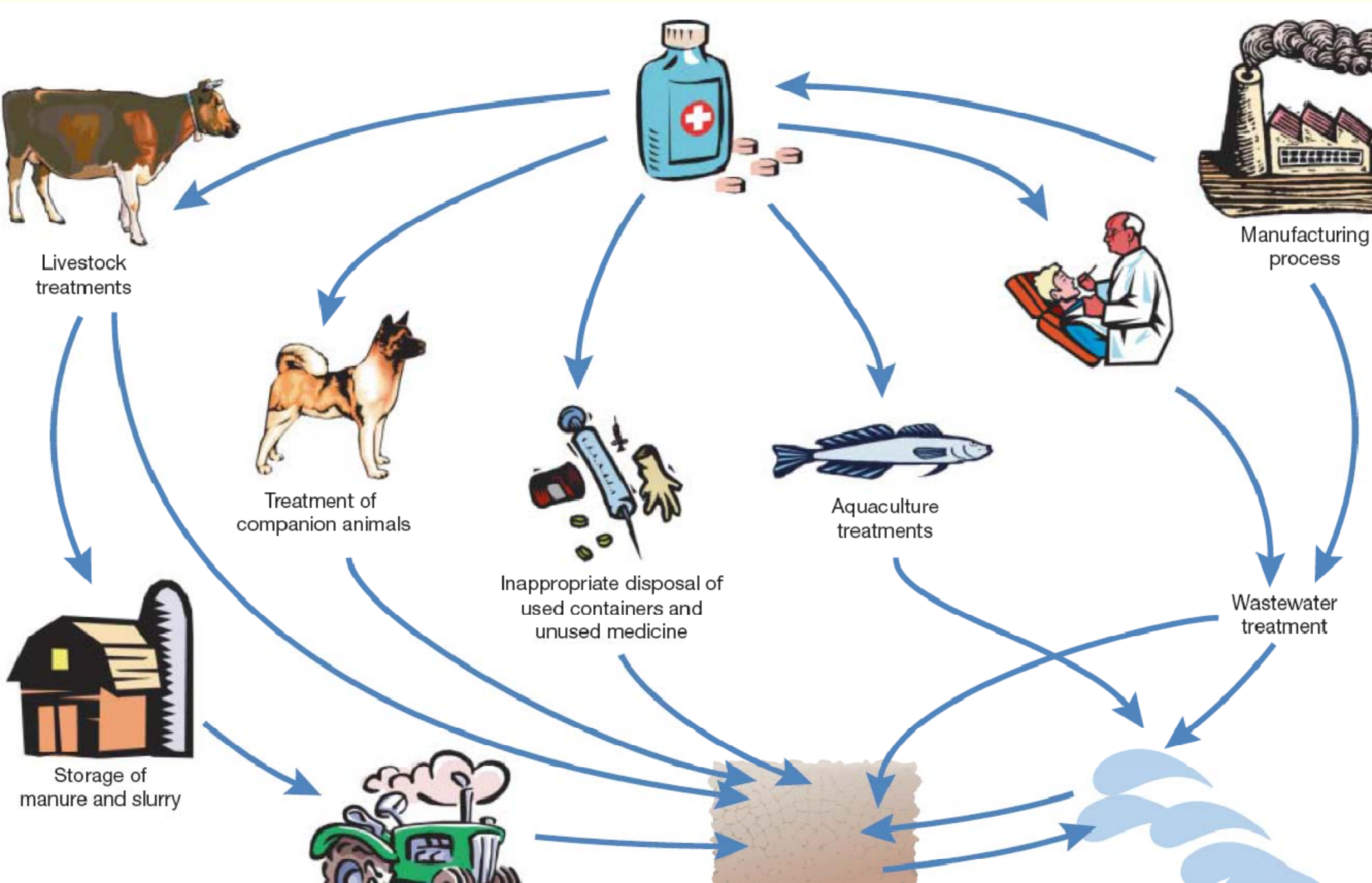
s

Plants not adapted for their removal

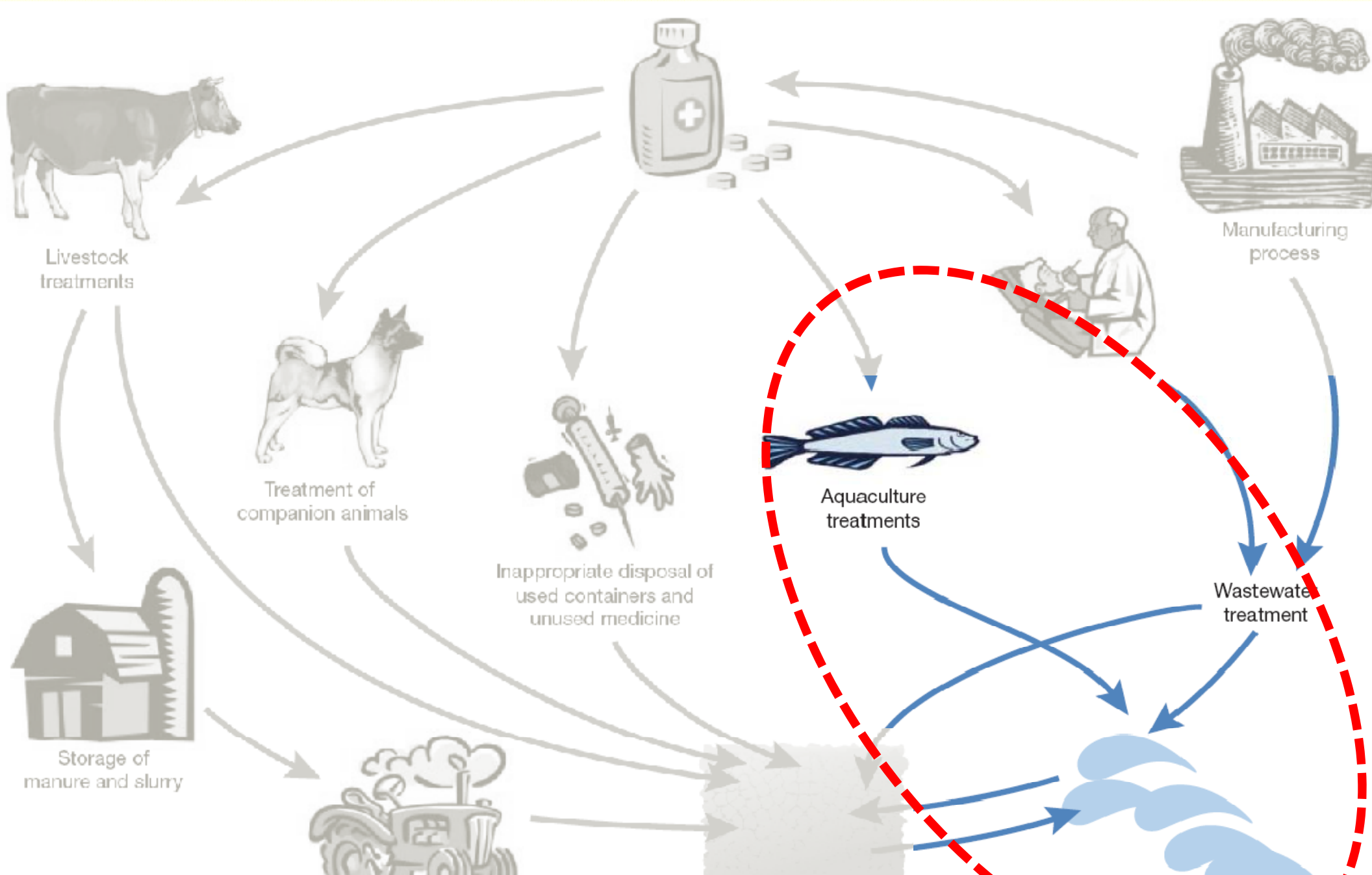
Diluted into the receiving wat

s

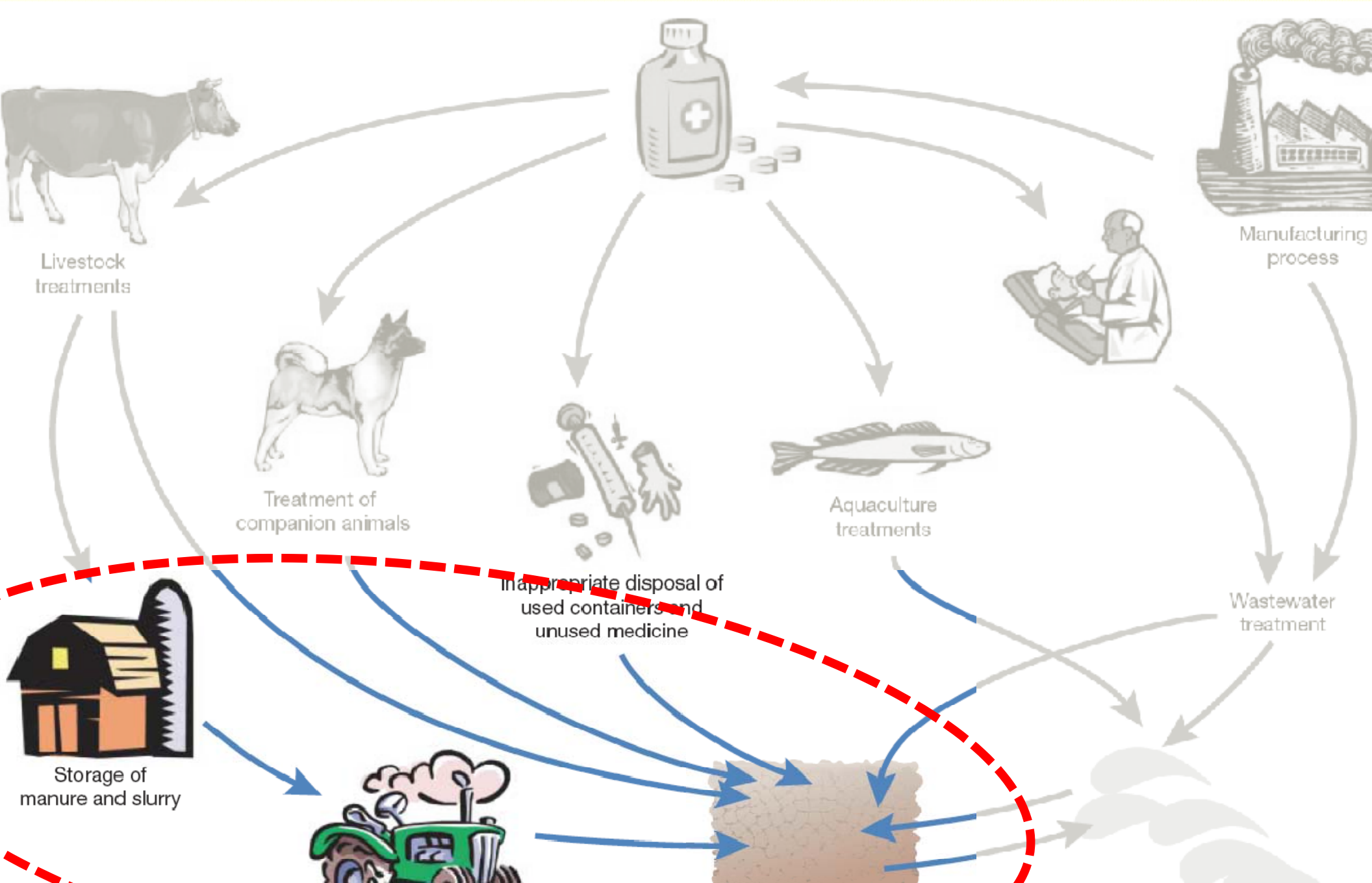
re are many sources and routes of pharmaceutica
oid hormones entering the environment.



t of the work done on these compounds is rela
r matrices.

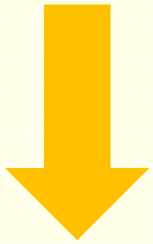


vever, it is now demonstrated that solid phases a
ficant importance and should be studied.

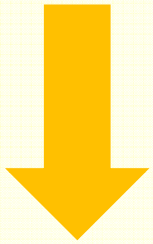


e in the environment, some of the endocrine disr
bounds (EDCs), such as steroidal hormones, may sorb to
onmental media and may persist for a long time.

e EDCs were detected in sites where municipal biosolids
applied.



s will potentially affect exposed biota and contamin
groundwater underlying sites and can eventually mak
way towards other water basins.



erefore, the need to develop analytical methods to quantify

Analytical challenges

ne consuming and labor-intensive extractio

- ✓ ultrasonic solvent extraction (USE)
- ✓ microwave assisted-extraction (MEA)
- ✓ pressurized liquid extraction (PLE)

trix complexity and interfering compounds

- ✓ solid phase extraction (prior to analysis by GC or
- ✓ nature, origin and composition of solid samples have an impact on extraction efficiency

e analysis of multiple classes of compou
h different physico-chemical properties wit
que method

This results in time consuming and labor intensive analytic

elop a **rapid** and **selective** analytical method ab
ct and quantify selected steroid hormones, paraben
rmaceuticals in multiple solid samples.

- **Rapid** = i) **L**aser **D**iode **T**hermal **D**esorption (LDT

  ii)reduced sample preparation (ultraso
  extraction with no SPE)

- **Selectivity** = **MS/MS**

LDTD is a sample introduction method that elim
need for liquid chromatography (LC) and allows a
ysis time of **15 sec/sample** instead of several mi

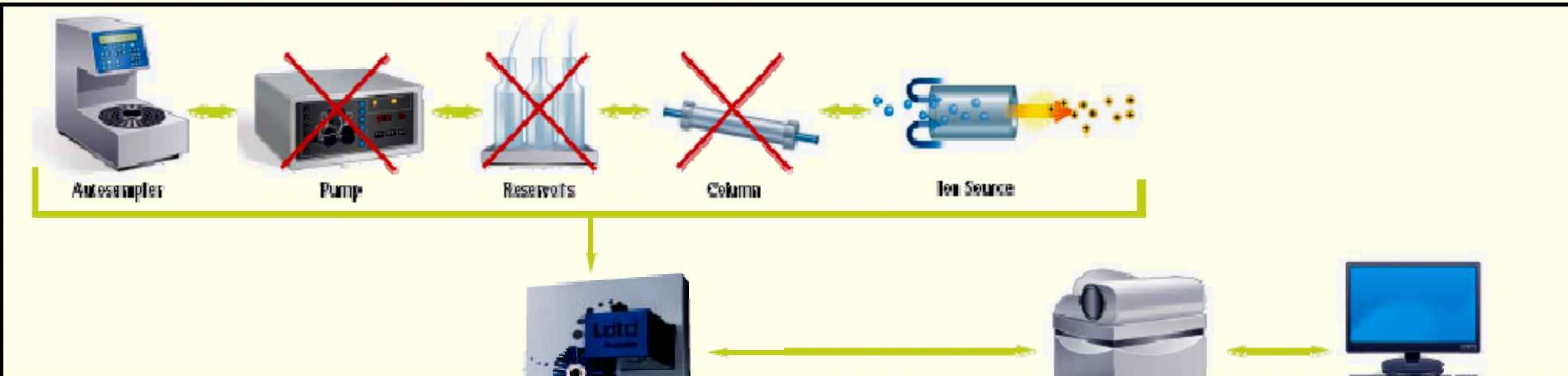
Analytical method: LDTD-APCI-MS/MS

ciples of the LDTD-APCI source:

chnique combining thermal desorption (laser diode) and APCI
mple is spotted (1-10 µL) into a 96-well plate; air-dried for 2 min
ncharged analytes are thermally desorbed into the gas phase
nization takes place in a corona discharge region by APCI

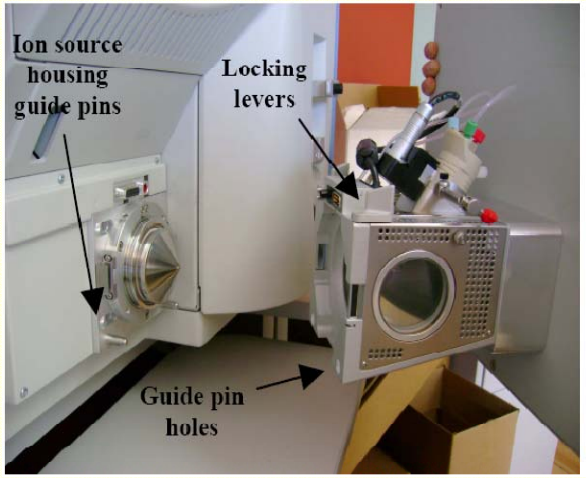
ntages of LDTD-APCI-MS/MS over LC-MS/MS:

nalysis is done in 15 sec versus several minutes in LC-MS/MS
mall sample volume (1-10 µL) versus on-line SPE-LC-MS/MS
ss contamination (tubing, column, injection loop or port, divert valv
wer costs (solvants, columns, tubing, syringes, pumps)



LDTD

Installation

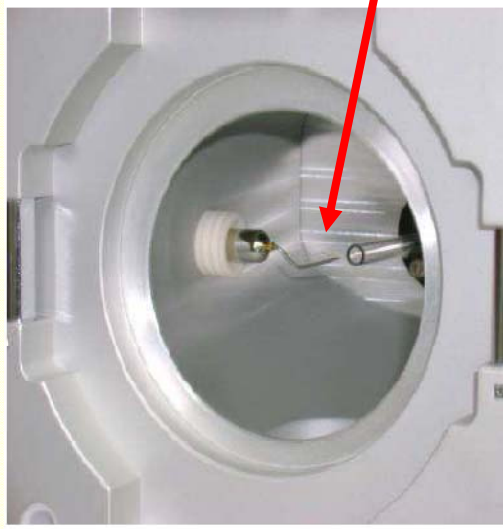


Auto-sampler

960 samples

IR Laser

(980 nm, 20 W)

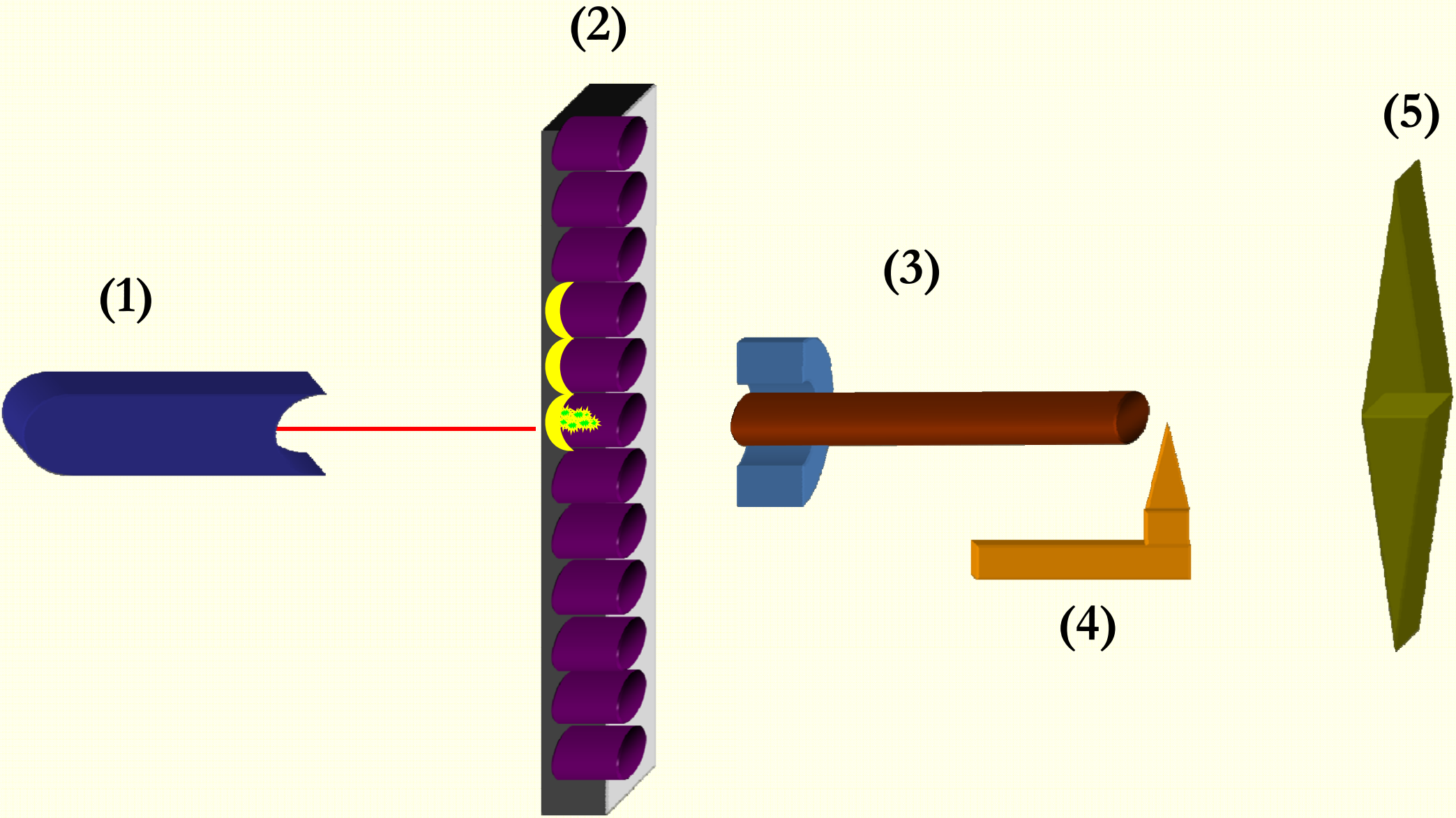


Corona needle posi

(APCI)

amp up to 3000°C/sec.

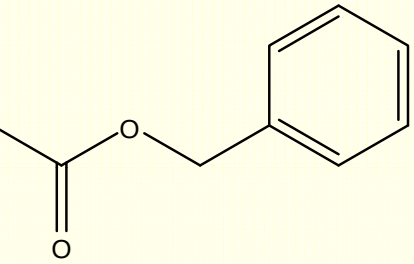
r power is defined in %



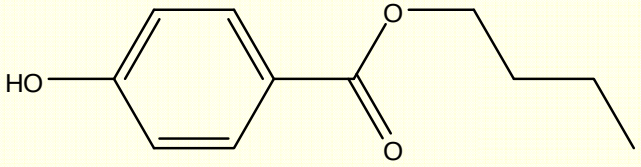
ed laser (980 nm, 20W)

ell Plate (96 wells): analyte desorption (1-10 µL spotted)

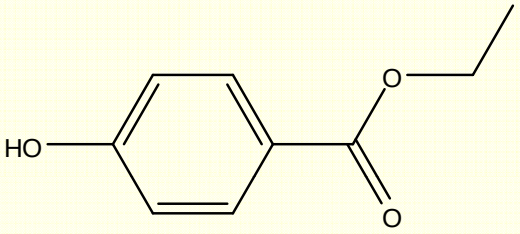
fer tube transporting the neutrally desorded analytes to the APCI region



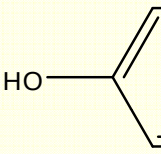
ylparaben



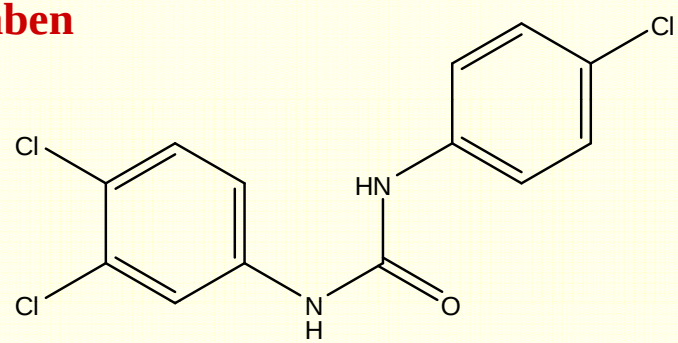
Butylparaben



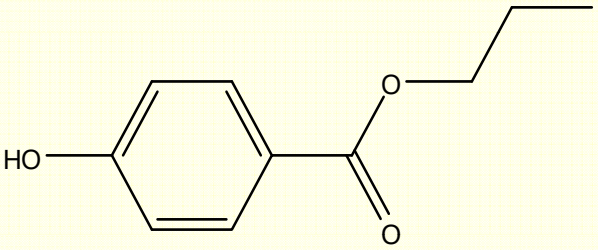
Ethylparaben



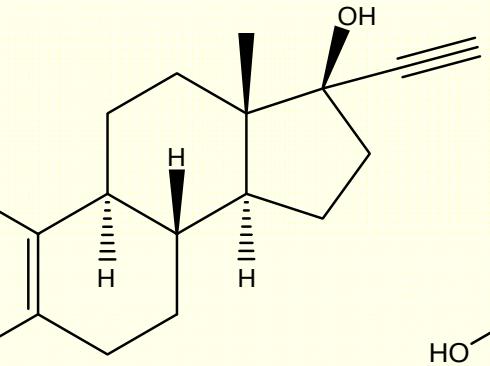
Meth



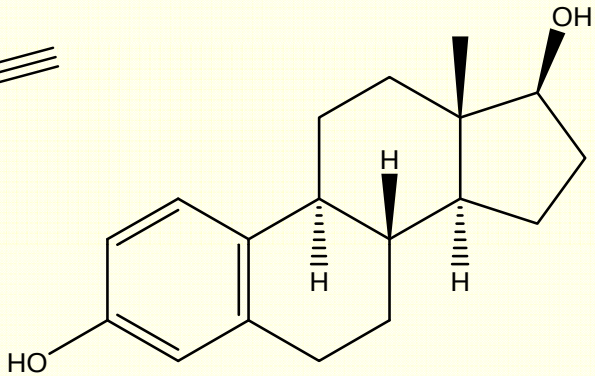
Triclocarban



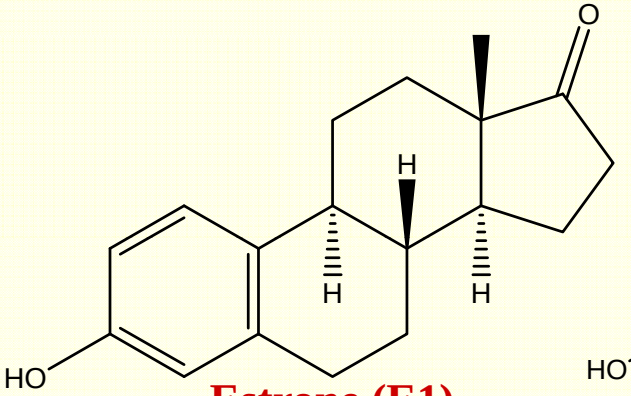
Propylparaben



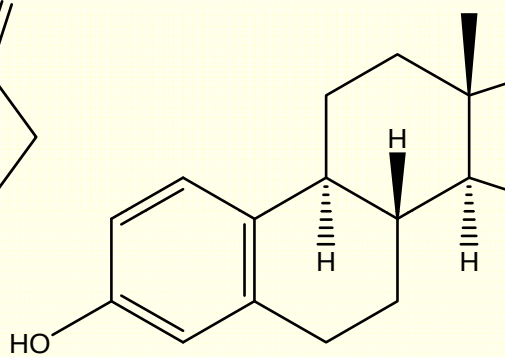
ynilestradiol (EE2)



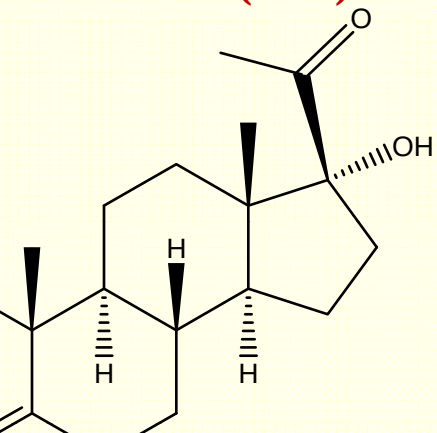
Estradiol (E2)

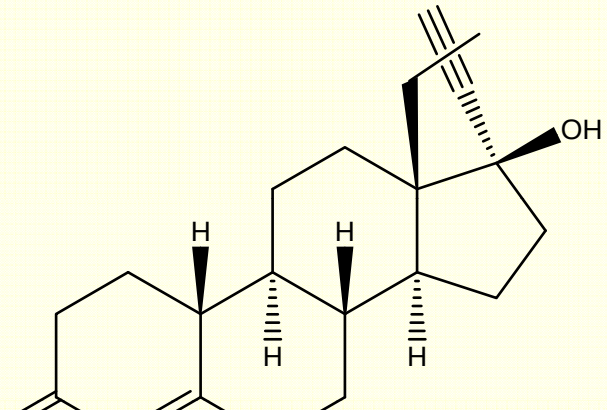


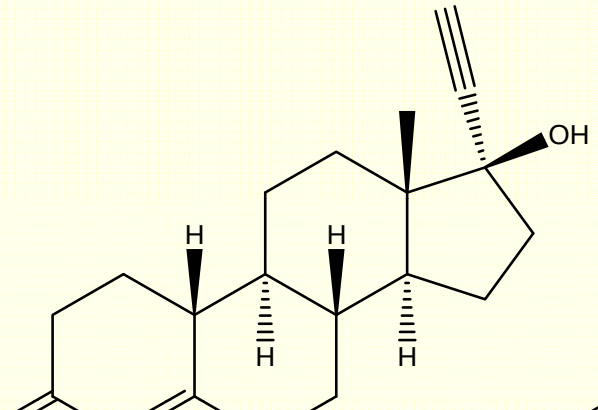
Estrone (E1)

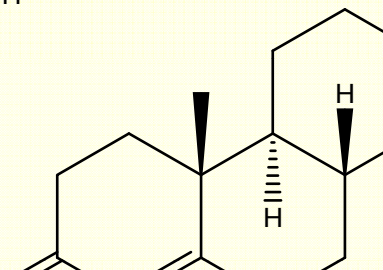


Estriol (E3)









OTD-APCI-MS/MS method optimizatio

re is no need for liquid chromatography optimizatio
aditional LC-MS/MS since it has been eliminated.

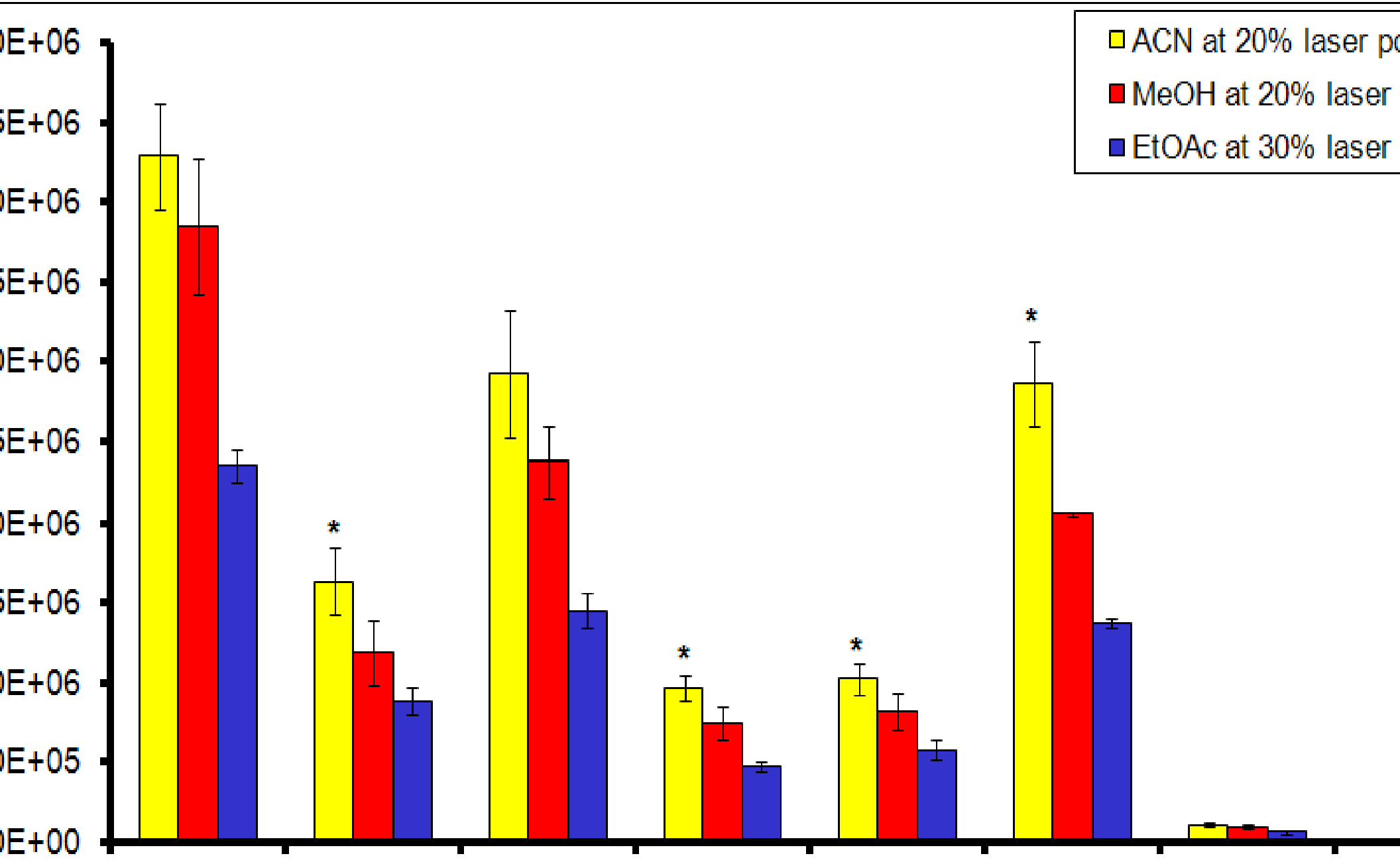
first step is sample optimization for MS (precurso
MS (SRM transitions) conditions in NI and PI mod

minimum of 2 SRM transitions were selected + their ion ra

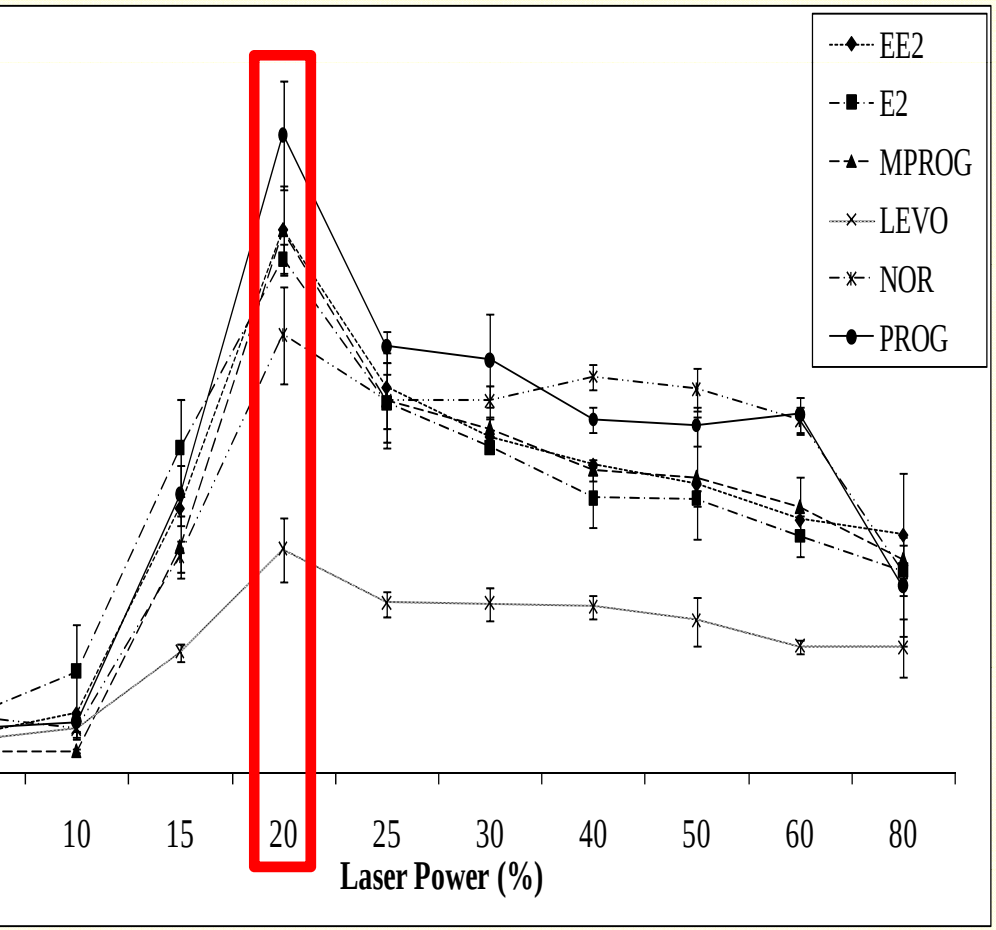
ical parameters of the LDTD-APCI source to
mized to improve signal intensity :

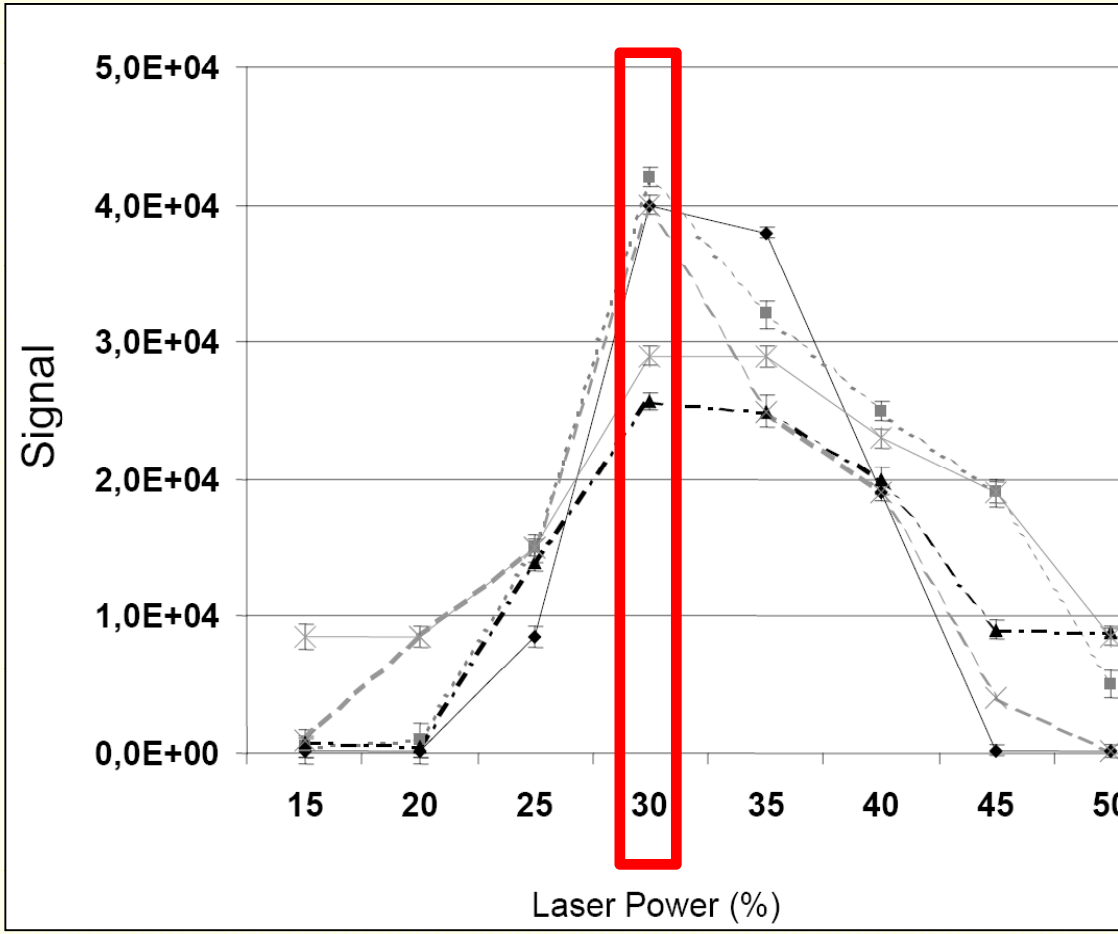
olvent choice for analyte deposition in the well cavities
aser power (%)
arrier gas flow (L/min)

ant choice for deposition: example for hormones
PI mode in matrix (effluent) at 2 mg/L, n=3.



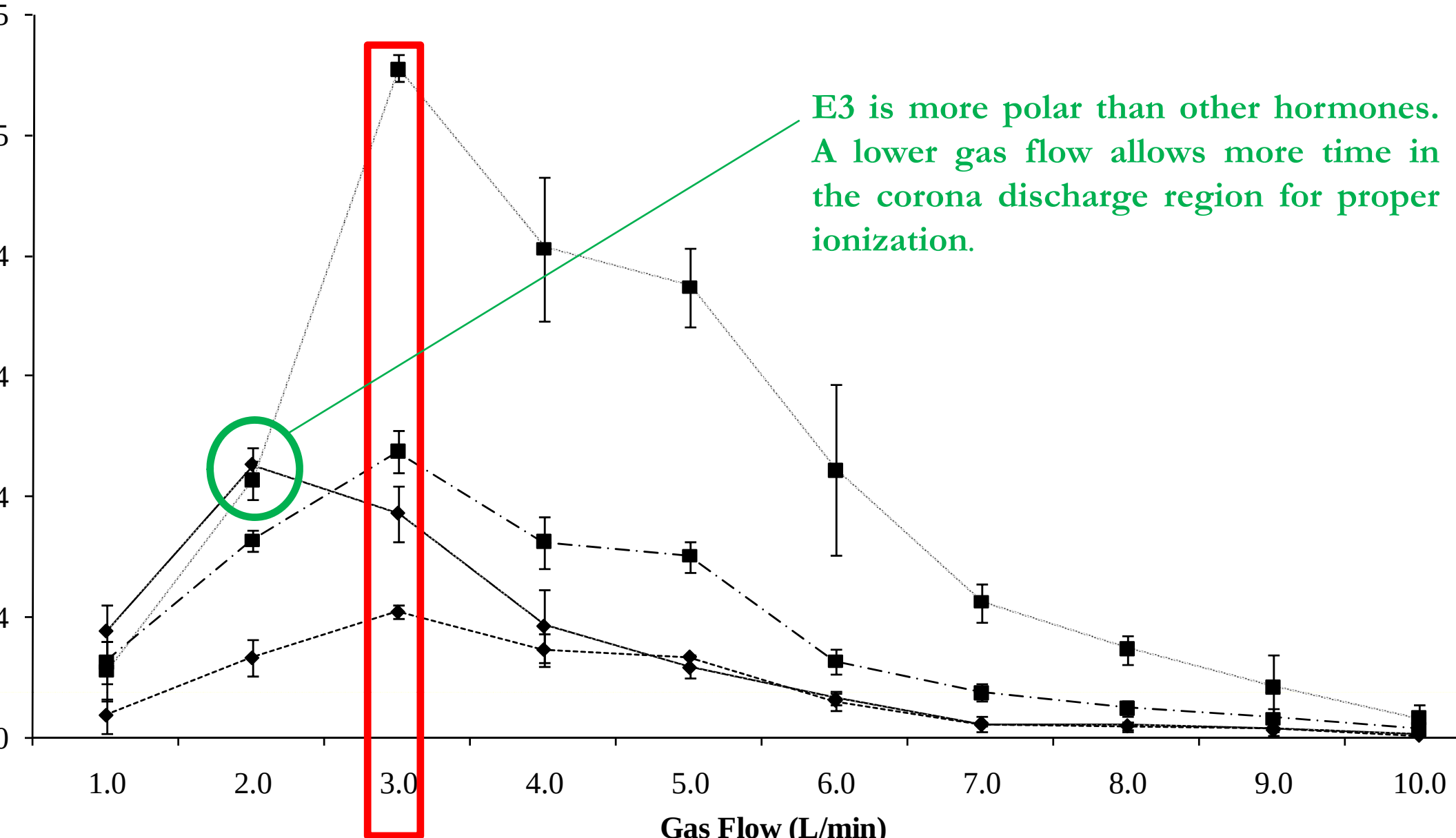
r power (%): example for hormones and parabens
e in matrix (effluent) at 2 mg/L, n=3.



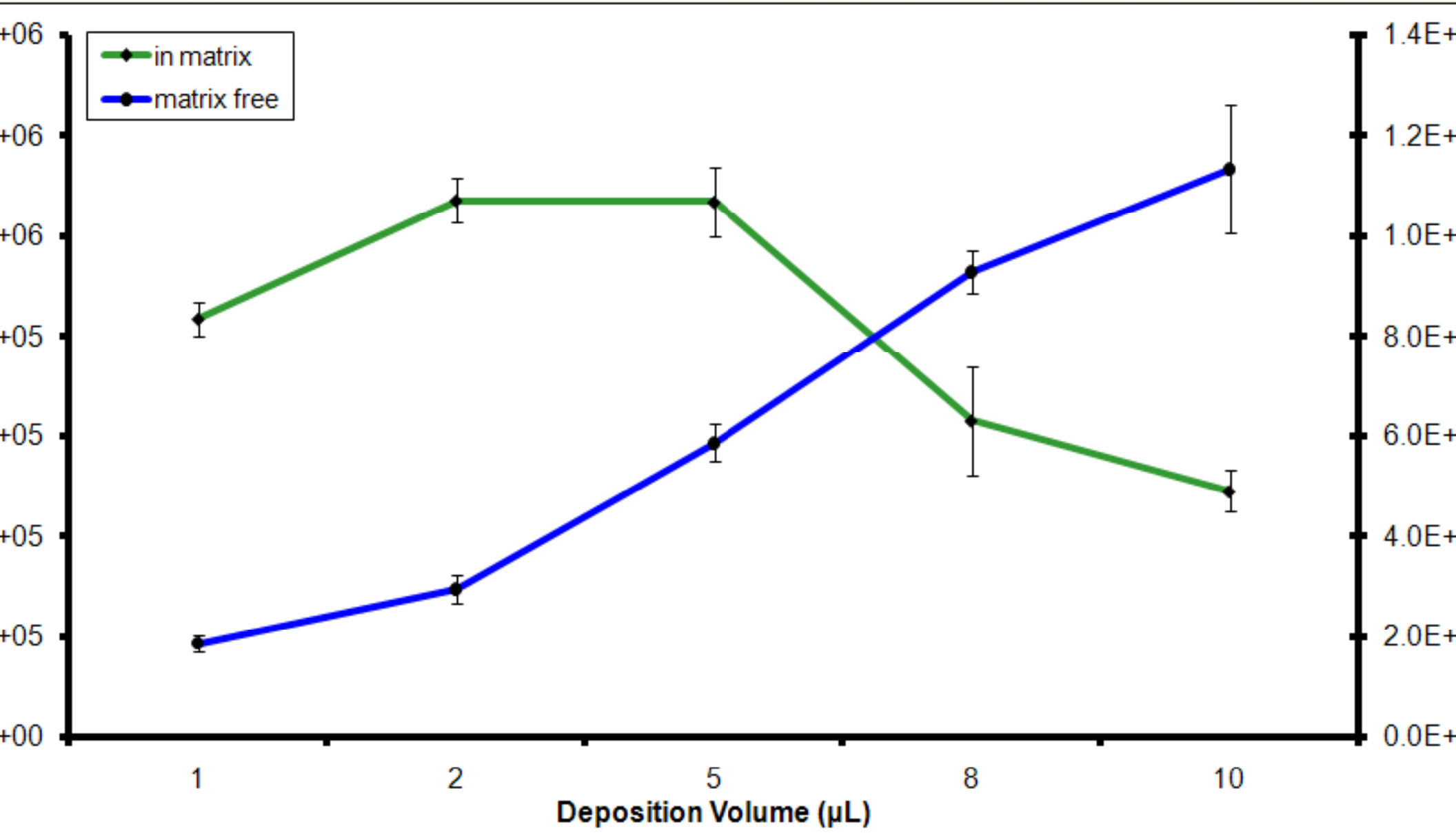


er power (%) is compound dependant and will
ording to affinity with the well plate surface, solve

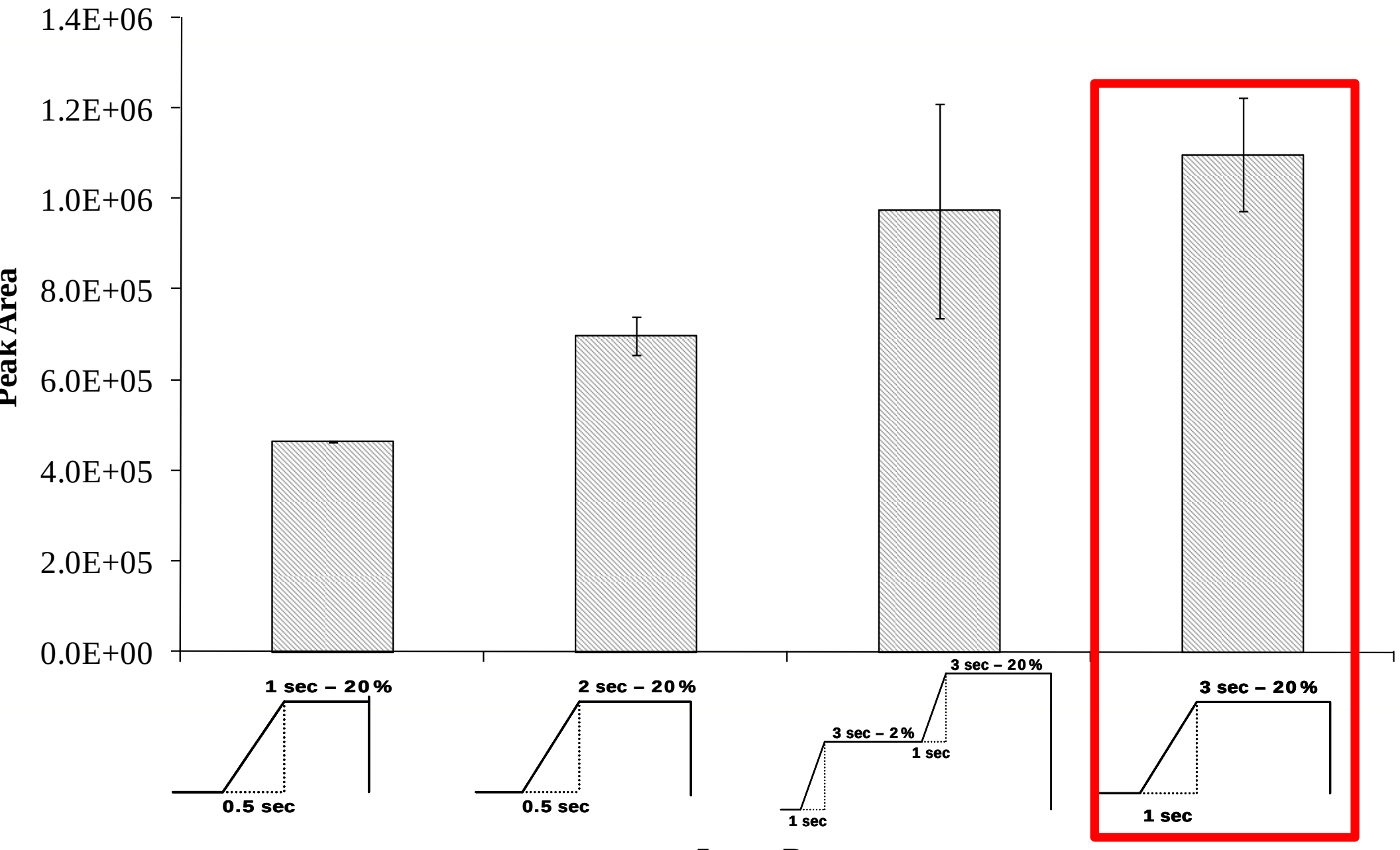
ier gas flow (L/min): example for hormones in NI
atrix (effluent) at 2 mg/L, n=3.



osition volume (µL): example for PROG in PI mo
ix (effluent) and neat solution at 2 mg/L, n=3.



r pattern: example for PROG in PI mode, in
uent) at 2 mg/L, n=3.



alytical method: extraction procedure and meth validation

action of solid phases (soil, sediments and sludge ca

:EtOAc (5:1 v/v)
+
sediment freeze-
r 0.2 g sludge

IS

shake vigorously
+
ultrasonic extraction
(30°C, 30 min)

wrist-shaker
(25°C, 45 min)
+
centrifugation
(1500*g*, 10 min)

evaporatio
the organ
(V_f = 0.

complet evaporation (N_2) of
the organic phase
+
reconstitution , 5 mL
Heptane:Acétone (65:35 v/v)

filtration on Silica cartridge
+
elution , 6 mL
Heptane:Acetone (65:35 v/v)

evaporation (N_2) of
the organic phase

Method detection limits (MDLs)
(ng/g)

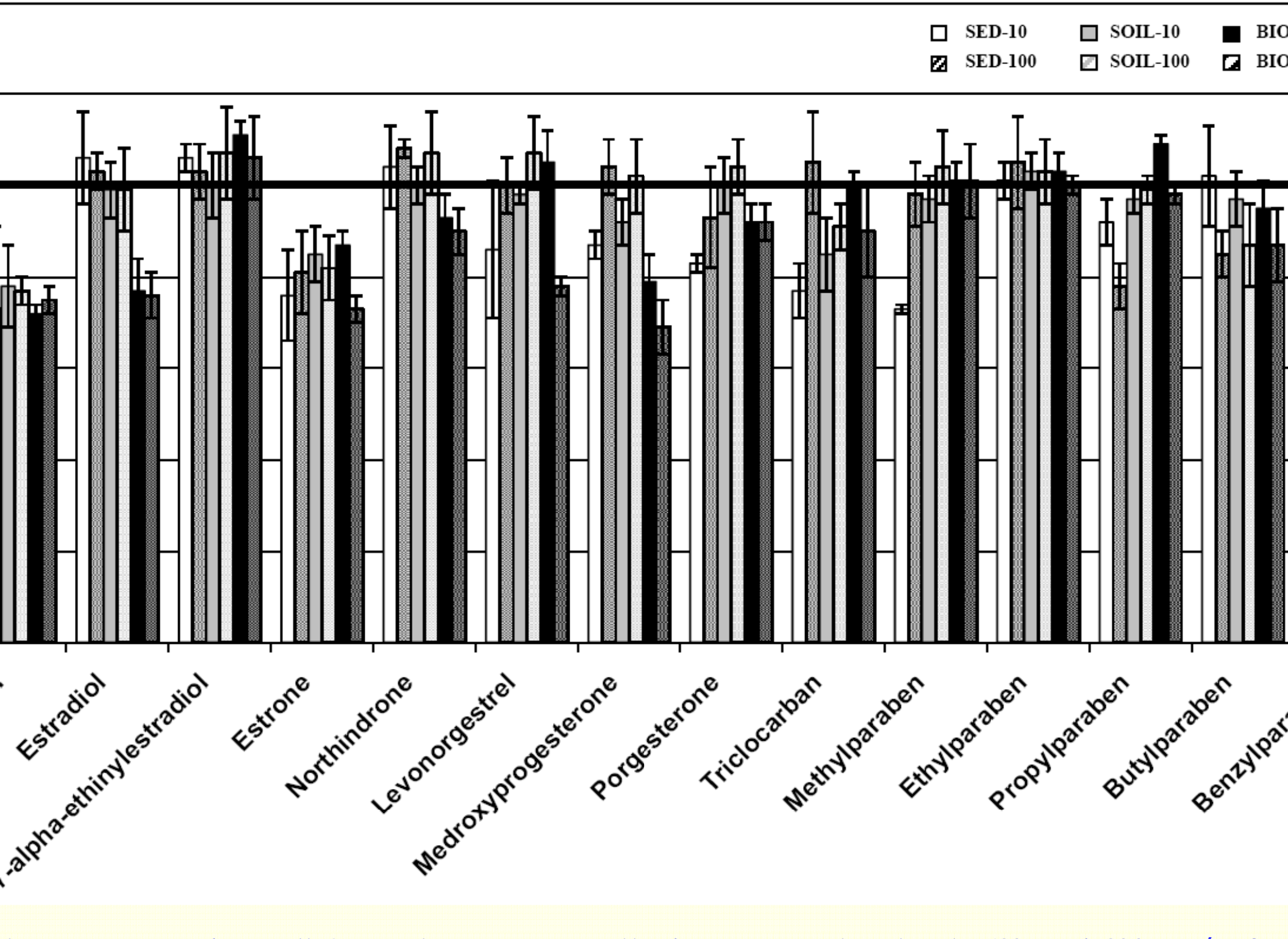
nd sediments		Sludge cakes	
nes	Parabens	Hormones	Parabens
.0	1.4 – 2.9	9.0 – 17	2.8 – 6.4

mmon procedure for soil/sediments and sludge cakes

ocedure for soil and sediments

lation parameters including linearity (R^2), repeatability, reproducibility and method detection limit (MDL, ng g

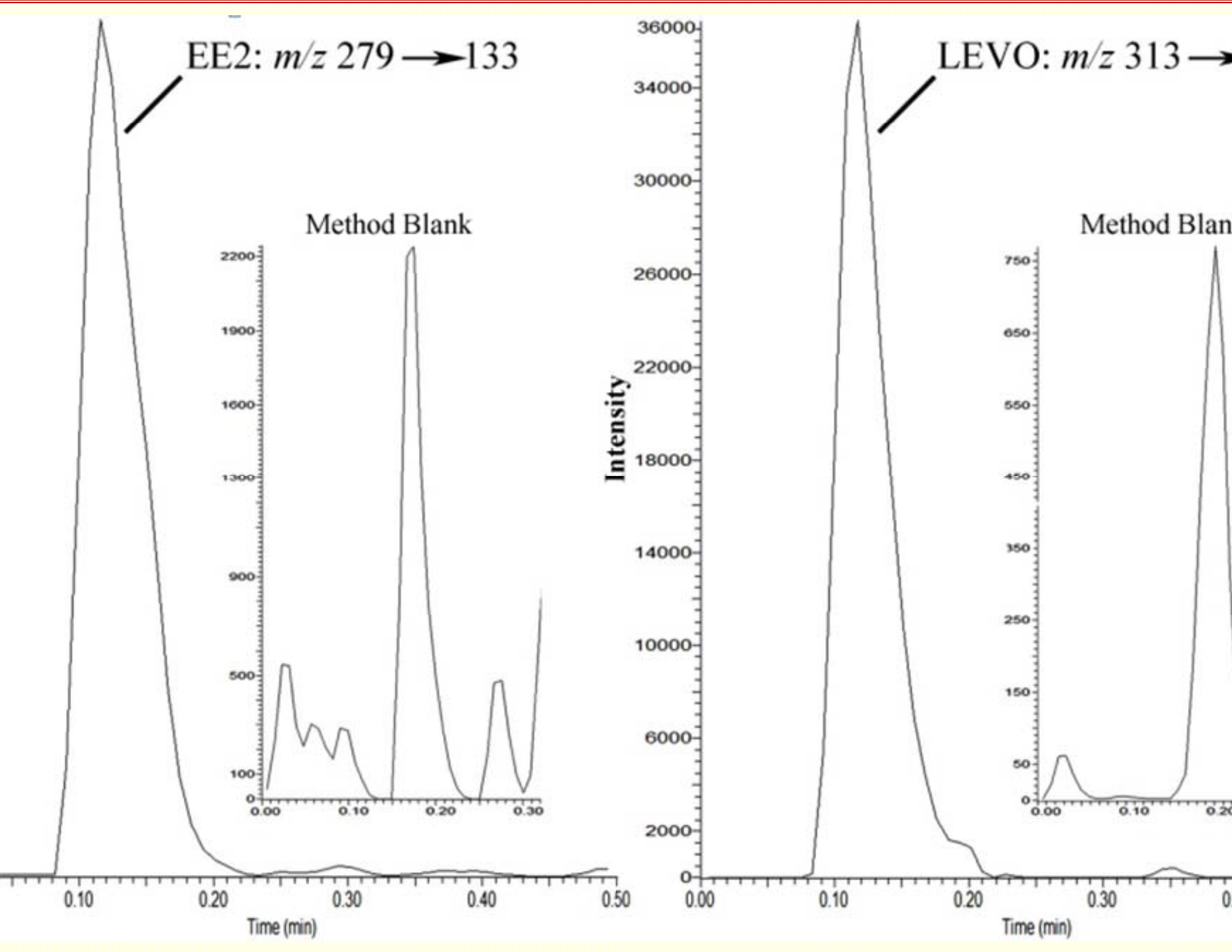
	SEDIMENTS				SOILS				BIOSOLIDS		
	R^2	Intra-day precision (% R.S.D.)	Inter-day precision (% R.S.D.)	MDL	R^2	Intra-day precision (% R.S.D.)	Inter-day precision (% R.S.D.)	MDL	R^2	Intra-day precision (% R.S.D.)	Inter prec (% R
	0.990	4	9	2.5	0.987	3	8	2.9	0.975	13	1
	0.998	7	11	4.0	0.990	5	8	3.0	0.962	8	1
	0.991	2	8	2.1	0.991	3	6	3.4	0.987	8	1
	0.995	2	8	3.2	0.990	3	7	3.2	0.998	11	9
	0.993	5	10	2.0	0.991	6	9	3.2	0.969	14	1
el	0.996	4	11	2.8	0.992	2	12	2.4	0.971	7	9
gesterone	0.996	4	8	0.9	0.990	3	8	1.4	0.966	5	9
	0.991	8	11	2.5	0.992	6	9	2.4	0.988	5	8
	0.997	3	7	0.7	0.991	4	5	2.9	0.973	9	1
en	0.982	2	6	1.3	0.987	3	3	1.6	0.974	3	7
	0.993	7	8	1.8	0.991	7	6	2.5	0.965	8	8
n	0.990	5	9	1.9	0.994	4	11	2.3	0.989	4	6
	0.982	9	9	1.6	0.989	7	8	1.9	0.987	4	7
n	0.981	10	6	2.8	0.983	9	11	2.5	0.980	6	6


SED-10
SOIL-10
BIO
SED-100
SOIL-100
BIO
Estradiol
-alpha-ethinylestradiol
Estrone
Northindrone
Levonorgestrel
Medroxyprogesterone
Porgesterone
Triclocarban
Methylparaben
Ethylparaben
Propylparaben
Butylparaben
Benzylpara

4. Mean concentration (mean ± SD, n = 3) of the selected compounds (ng g^{-1}) in sediments (SEDIMENT-I an

SOIL-II and III) and municipal sludge cakes (Biosolid-I and II).

	SEDIMENTS		SOILS		BIOSOLIDS	
	I	II	II	III	I	II
l	18 ± 3	6 ± 3	15 ± 3	28 ± 9	69 ± 3	45 ±
diol	70 ± 7	22± 4	93 ± 12	81 ± 11	57 ± 3	41 ±
ha-ethinylestradiol	30 ± 6	n.d	86 ± 12	34 ± 11	55 ± 3	47 ±
ne	16 ± 6	6 ± 3	7 ± 2	10 ± 2	54 ± 3	32 ±
hindrone	90 ± 9	n.d	93 ± 17	91 ± 22	106 ± 3	105 ±
orgestrel	19 ± 5	n.d	24 ± 12	52 ± 17	53 ± 3	33 ±
oxyprogesterone	29 ± 3	n.d	28 ± 4	13 ± 3	31 ± 3	22 ±
sterone	12 ± 4	≤ LMD	31 ± 9	19 ± 6	89 ± 3	72 ±
	16 ± 4	n.d	53 ± 9	13 ± 2	59 ± 3	43 ±
lparaben	56 ± 7	n.d	127 ± 12	107 ± 4	72 ± 2	91 ±
paraben	12 ± 2	n.d	≤ LMD	15 ± 3	≤ LMD	n.d
lparaben	15 ± 4	n.d	5 ± 2	9 ± 1	8 ± 1	n.d
paraben	19 ± 3	n.d	20 ± 5	23 ± 4	≤ LMD	n.d


EE2: m/z 279 → 133
Method Blank
LEVO: m/z 313 →
Method Blan
Intensity
Time (min)
Time (min)

DTD-APCI-MS/MS method was develop for the rapid (15 sec/s
ion and quantification of selected steroid hormones and parab
different solid matrices (soil, sediments and sludge cakes).

proved (less time and labor-intensive than previous methods) ext
od for all three matrices was applied using only an ultrasonic ext
simple clean-up procedure added for the sludge cakes because of
exity.

work demonstrates the possibility of applying high-throughput a
ltiple compounds in solid matrices of different origins.

ervisors:

Sébastien Sauvé, *Ph.D.* (Université de Montréal)

et

Michelle Prévost, *Ph.D.* (École Polytechnique de Montréal)

Phytronix Technologies

Thermo SCIENTIFIC

CHAIRE INDUSTRIELLE CRSNG EN EAU POTABLE

act me at paul.fayad@umontreal.ca for more details.