Interaction of alkylphenolic and perfluorinated compounds with sewage sludges and soils

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Interaction of alkylphenolic and perfluorinated compounds with sewage sludges and soils

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Interaction of alkylphenolic and perfluorinated compounds with sewage sludges and soils

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El Dr. **Miquel Vidal**, catedràtic del Departament de Química Analítica de la Universitat de Barcelona, i la Dra. **Anna Rigol**, professora titular del Departament de Química Analítica de la Universitat de Barcelona,

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TABLE OF CONTENTS

CHAPTER 3. INTERACTION OF ALKYLPHENOLIC COMPOUNDS WITH SEWAGE SLUDGES AND SOILS 93

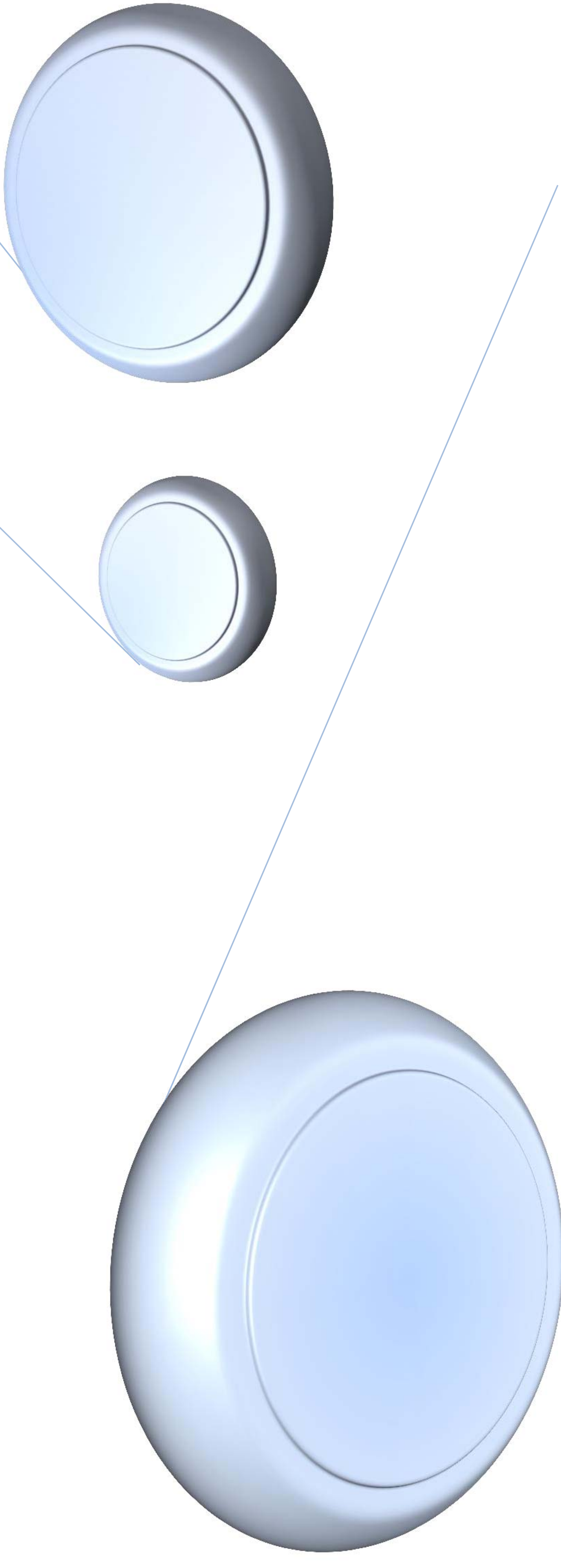
LIST OF ABBREVIATIONS

AP	Alkylphenol
APEC	Alkylphenol carboxylate
APEO	Alkylphenol ethoxylate
APC	Alkylphenolic compound
BPA	Bisphenol A
CAS	Chemical Abstracts Service
CEC	Cation exchange capacity
CEN	European Committee for Standardization
$\mathbf{C_{eq}}$	Concentration of the substance in the contact liquid phase after sorption
$\mathbf{C_{eq,des}}$	Concentration of the substance in the contact liquid phase after desorption
$\mathbf{C_{in}}$	Initial concentration of the substance in the sorption experiment
$\mathbf{C_{in,des}}$	Initial concentration of the substance in the desorption experiment
$\mathbf{C_{s}}$	Concentration of the substance sorbed at the solid phase after sorption
$\mathbf{C_{s,des}}$	Concentration of the substance remaining sorbed at the solid phase after desorption
D	Desorption yield
dm	Dry matter
DOC	Dissolved organic carbon
EC	European Commission
EDAR	Estación depuradora de aguas residuales
EDC	Endocrine disrupting chemicals
EEC	European Economic Community

EPA	Environmental Protection Agency
Eq.	Equation
EU	European Union
FAO	Food and Agriculture Organization
F_{OC}	Fraction of organic carbon
FT-IR	Fourier transform infrared
GC	Gas chromatography
ICP-OES	Inductively coupled plasma optical emission spectrometry
IS	Internal standard
ISO	International Organization for Standardization
K_d	Sorption solid-liquid distribution coefficient
$K_{d,des}$	Desorption solid-liquid distribution coefficient
$K_{d,linear}$	Sorption solid-liquid distribution coefficient derived from the slope of the linear sorption isotherm
$K_{d,max}$	Maximum sorption solid-liquid distribution coefficient
$K_{d,min}$	Minimum sorption solid-liquid distribution coefficient
$K_{d,MIN}$	Solid-liquid distribution coefficient at the mineral fraction
$K_{d,ORG}$	Solid-liquid distribution coefficient at the organic fraction
K_F	Freundlich constant for the sorption
$K_{F,des}$	Freundlich constant for the desorption
K_{OC}	Solid-liquid distribution coefficient referred to organic carbon
K_{OW}	Octanol-water partition coefficient
LAS	Linear alkylbenzene sulfonate
LC	Liquid chromatography
LLE	Liquid-liquid extraction
LOD	Limit of detection
$LOD_{instr.}$	Limit of detection of the instrument

LOD_{method}	Limit of detection of the method
MPFOA	Perfluoro-(1,2,3,4-$^{13}C_4$)-octanoic acid
MPFOS	Perfluoro-(1,2,3,4-$^{13}C_4$)-octanesulfonic acid
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
Mw	Molecular weight
m/z	Mass-to-charge ratio
N	Freundlich parameter for the sorption
na	Not analyzed
nd	Not detected
N_{des}	Freundlich parameter for the desorption
NMR	Nuclear magnetic resonance
NP	Nonylphenol
NP-D8	Nonylphenol D8
NP_1EO	Nonylphenol-mono-ethoxylate
NP_1EO-D2	Nonylphenol-mono-ethoxylate D2
NP_2EO	Nonylphenol-di-ethoxylate
OC	Organic carbon
OECD	Organization for Economic Cooperation and Development
OM	Organic matter
OP	Octylphenol
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PFBS	Perfluorobutane sulfonate
PFC	Perfluorinated compound
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexane sulfonate

PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
POC	Particulate organic carbon
POP	Persistent organic pollutant
rdw	Respect to dry weight
rpm	Revolutions per minute
RSD	Relative standard deviation
S	Sorption percentage
SD	Standard deviation
SE	Standard error
SIM	Selected ion monitoring
TOC	Total organic carbon
$\mathbf{t_R}$	Retention time
USDA	United States Department of Agriculture
$\mathbf{V_{res}}$	Residual volume of solution
WWTP	Wastewater treatment plant
XRD	X-ray diffraction



Resumen

Objetivo

El objetivo principal de esta tesis doctoral ha sido estudiar la interacción de contaminantes orgánicos persistentes, tales como compuestos alquilfenólicos (APCs) y perfluorados (PFCs) con lodos de depuradora y muestras de suelo. Este objetivo principal se puede desglosar en tres objetivos específicos:

1) Examinar la lixiviación de APCs en lodos de depuradora procedentes de diferentes plantas de tratamiento de aguas residuales, y evaluar el efecto del tratamiento de secado de los lodos en la lixiviación de estos contaminantes.

2) Estudiar el comportamiento de sorción de APCs en muestras de suelo con distintas características y elucidar los mecanismos responsables de la interacción APC-suelo.

3) Investigar el comportamiento de sorción de PFCs en muestras de lodo de depuradora y de suelo, así como determinar las principales propiedades fisicoquímicas de los compuestos y de las muestras que que controlan esta sorción.

Con la obtención de parámetros de sorción y desorción para estos compuestos en estas matrices ambientales, así como a partir de la interpretación de los factores que afectan a estos procesos, se pretende contribuir a la mejora de la predicción del comportamiento de estas dos familias de compuestos en lodos y suelos.

Introducción

La aplicación de las Directivas 91/271/CEE y 98/15/EEC, sobre el tratamiento de aguas residuales urbanas para la protección del medio ambiente, ha conllevado, en los últimos años, un aumento progresivo en el número de estaciones depuradoras de aguas residuales (EDAR) y, en consecuencia, en la generación de lodos resultantes de su actividad. Con el fin de reutilizar los nutrientes y materia orgánica que contienen estos lodos, y de minimizar su eliminación a vertedero, una de las rutas más empleadas en la gestión de estos lodos, en algunos países, es su reutilización en agricultura. Este es el caso de algunos países europeos como Dinamarca, Francia, Reino Unido y España, que reutilizan más de la mitad de los lodos generados en las EDAR como fertilizante en suelos agrícolas. Esta práctica debe llevarse a cabo de tal manera que se reduzca al mínimo el riesgo de efectos nocivos para la salud humana y los ecosistemas, manteniendo la calidad de las aguas subterráneas, las aguas superficiales y los suelos.

Los lodos de depuradora, aparte de su elevado contenido en nutrientes y materia orgánica, son acumuladores potenciales de sustancias peligrosas, en especial de compuestos orgánicos hidrofóbicos, por lo que repetidas aplicaciones de estos lodos en suelos podrían conllevar la incorporación de contaminantes a concentraciones de riesgo para la salud humana y los ecosistemas. En este sentido, la aplicación de lodos de depuradora en los suelos agrícolas está regulada por la Directiva 86/278/CEE, que establece los valores límites relativos a las concentraciones de metales pesados en los suelos, en los lodos, y a las cantidades máximas anuales de estos metales pesados que pueden ser introducidas en los suelos destinados a la agricultura. Sin embargo, no incorpora, de momento, valores límite de contaminantes orgánicos, por lo que en el contexto del proceso de revisión de la presente Directiva, se ha considerado la necesidad urgente de obtener información sobre la presencia de contaminantes orgánicos emergentes en los lodos de depuradora que van a ser reutilizados en agricultura. Algunos documentos desarrollados por la Unión Europea proponen valores límite para las concentraciones de algunas familias de compuestos orgánicos en los lodos. Entre ellos, el valor máximo propuesto para la suma de nonilfenol (NP), nonilfenol mono-etoxilado (NP_1EO) y nonilfenol di-etoxilado (NP_2EO) fue, en un primer documento, de 50 mg kg^{-1} y, más recientemente, de 450 mg kg^{-1}. Estos compuestos son productos de degradación de compuestos alquilfenólicos más complejos, que se forman durante el proceso de digestión de los lodos llevado a cabo en las EDAR. Presentan un carácter hidrofóbico y son más resistentes a la biodegradación que sus precursores. Por otra parte, se considera que causan disrupción endocrina, ya que pueden interferir en el funcionamiento normal de los sistemas hormonales. Entre los

APCs, el 4-t-octylfenol (OP), aunque no figura en las propuestas de modificación de la Directiva 86/278/CEE, fue incluido en la lista de sustancias peligrosas prioritarias debido a su toxicidad y persistencia.

Otra familia de compuestos orgánicos que se han detectado en las aguas residuales y en diferentes fases del tratamiento de estas aguas en las EDAR, son los compuestos perfluorados (PFCs). Esto indica que estos compuestos no se degradan totalmente en el proceso y, por lo tanto, una fracción significativa puede acumularse en los lodos de depuradora. Entre todos los PFCs, el sulfonato de perfluorooctano (PFOS) y el ácido perfluorooctanoico (PFOA) son los que muestran una mayor acumulación en el medio ambiente. PFOS y sus sales se encuentran en la lista de contaminantes orgánicos persistentes del Convenio de Estocolmo, por lo que la Comunidad Europea ha prohibido su uso y fabricación. Más recientemente, el sulfonato de perfluorobutano (PFBS) ha sido comercializado como sustituto del PFOS en una variedad de aplicaciones, por ser menos tóxico.

Para evaluar el riesgo asociado a la contaminación de lodos y suelos debido a los contaminantes orgánicos, no sólo debe considerarse la concentración total de los contaminantes en estas matrices, sino también su interacción con los componentes sólidos de éstas, tanto des del punto de vista de la sorción de los compuestos como de la reversibilidad de esta sorción. En el caso de APCs la información acerca de su lixiviación en lodos y de la influencia de algunos factores, como el secado, en esta lixiviación es limitada. Así mismo, existe poca información sobre el comportamiento de sorción de APCs en suelos y básicamente se centra en el NP.

Por lo que se refiere a PFCs, existen algunos trabajos previos sobre su sorción en lodos, pero los valores de K_d obtenidos pueden variar hasta tres órdenes de magnitud en función del lodo y del compuesto. Por lo que se refiere a suelos, los valores de K_d encontrados también pueden variar en dos órdenes de magnitud. Por otra parte, no hay datos disponibles acerca de la reversibilidad de la sorción de PFCs en suelos y lodos, aunque existen algunos datos de K_d *in situ* en lodos de depuradora y materia en suspensión.

En la presente tesis, se estudió la interacción de dos familias de compuestos, APCs y PFCs, en muestras de interés ambiental, en el contexto del sistema terrestre, como son los lodos de depuradora y los suelos. En la primera parte de la tesis, se evaluó la lixiviación de algunos APCs, como OP, NP y NP_1EO, en cinco muestras de lodos de depuradora, examinando la influencia que el secado de la muestra podría tener en esta lixiviación. Por otra parte, se estudió el comportamiento de sorción de NP y NP_1EO en cinco muestras de suelo con diferentes propiedades edáficas, tales como el carbono orgánico y el carbono orgánico disuelto. Se realizaron ensayos de sorción a distintas concentraciones del compuesto a estudiar con el fin de obtener las isotermas correspondientes que, una vez ajustadas a los modelos de Freundlich y lineal, permitieron deducir las mejores estimaciones del valor del coeficiente de distribución sólido-líquido (K_d) de APCs en suelos. De forma similar se obtuvieron isotermas de desorción para evaluar la reversibilidad de la sorción. Finalmente, se examinó la influencia de las características de los lodos y los suelos, así como de las propiedades fisicoquímicas de los APCs, en el patrón de lixiviación y sorción observado.

En la segunda parte de la tesis se examinó, de forma similar al caso anterior, la sorción de PFCs en lodos y suelos, así como la reversibilidad de esta sorción, con la finalidad de establecer los mecanismos que controlan estos procesos. Para ello, se obtuvieron isotermas de sorción y desorción para tres PFCs con distintas estructuras y propiedades fisicoquímicas, PFOS, PFOA y PFBS. Al igual que para APCs, se ajustaron las isotermas correspondientes y se obtuvieron las mejores estimaciones de los valores de K_d para cada combinación PFC-lodo y PFC-suelo. Además, se examinaron las correlaciones entre los parámetros de sorción y desorción y las principales propiedades fisicoquímicas de las matrices en estudio y/o de los compuestos.

Materiales y métodos

Muestras de lodos de depuradora

Se tomaron cinco muestras de lodos de depuradora (SL1 - SL5) en EDARs localizadas en diferentes zonas industriales de Cataluña. Cada muestra de lodo se homogeneizó y se dividió en dos porciones. Una porción se mantuvo a -18 °C sin ningún tratamiento adicional y se designó como muestra de lodo fresco. La otra porción se secó a 40 °C, se mantuvo a temperatura ambiente y se designó como muestra de lodo seco. Para el estudio de lixiviación de APCs se utilizaron las cinco muestras de lodo fresco y seco, mientras que para la evaluación del comportamiento de sorción de los PFCs, se emplearon cuatro de las muestras de lodo seco (SL1, SL3, SL4 y SL5). Las principales características fisicoquímicas de las muestras de lodo seco, se resumen en la Tabla 1.

Como se puede observar, las muestras SL1, SL2 y SL3 presentaban un pH similar, siendo éste ligeramente básico, mientras que el de la muestra SL4 era neutro, y finalmente el de la muestra SL5 era ligeramente ácido. El contenido de Ca+Mg en los lixiviados, fue inversamente proporcional al pH y directamente proporcional a la materia orgánica (OM). Los valores de contenido de carbono orgánico (OC) variaron desde 23 a 37% entre las cinco muestras de lodo. Los valores del carbono orgánico disuelto (DOC) y del pH de las muestras de lodo fueron inversamente proporcionales, lo que sugirió que el incremento en la concentración de compuestos orgánicos solubles causó una disminución en el pH de las muestras de lodos.

Tabla 1. Principales características fisicoquímicas de las muestras de lodos de depuradora (valor medio (desviación estándar); n=3)

Lodo	**Materia seca (%)**	**pH**	**OM (%)**	**C^a (%)**	**N^a (%)**	**OC (%)**	**Ca (mmol kg^{-1})**	**Mg (mmol kg^{-1})**	**DOC (mg kg^{-1})**
SL1	21,0 (0,2)	8,3 (0,1)	61,6 (0,1)	34,3	5,3	27,9 (0,2)	31 (3)	32 (1)	35900 (60)
SL2	28,7 (0,1)	8,6 (0,1)	50,4 (0,6)	38,5	7,6	32,2 (0,1)	50 (4)	20 (1)	21400 (400)
SL3	17,2 (0,1)	8,4 (0,1)	62,5 (0,8)	34,9	7,1	28,2 (0,3)	24 (3)	21 (1)	53000 (1100)
SL4	13,9 (0,1)	7,1 (0,1)	73,2 (0,1)	28,5	3,9	22,8 (0,1)	50 (1)	38 (2)	70000 (2400)
SL5	16,1 (0,1)	6,1 (0,1)	77,4 (0,2)	41,5	6,9	37 (1)	54 (1)	86 (4)	70000 (2400)

[a] n = 1

Muestras de suelos

En la presente tesis se utilizaron seis muestras de suelo (ASCO, ALM, GOLOSO, DELTA2, OVI01, DUBLIN), procedentes de una colección de suelos del grupo de investigación, correspondientes a la capa superior de 10 cm. Las principales propiedades de los suelos se muestran en la Tabla 2.

Varios suelos presentaron un pH ácido (ALM, GOLOSO, OVI01 y DUBLIN) con $CaCO_3$ inferior al 4%, mientras que los suelos ASCO y DELTA2 fueron básicos, con un alto contenido de $CaCO_3$. El contenido de carbono orgánico (OC) varió en más de dos órdenes de magnitud (de 0,2% en ASCO hasta un 39% en DUBLIN). El contenido de carbono orgánico disuelto (DOC) varió de 184 en ASCO hasta 5741 mg kg^{-1} en OVI01. El suelo DUBLIN presentó el mayor contenido de OC, pero uno de los valores más bajos del DOC, lo que resultó en una muy baja proporción DOC/OC.

La relación más alta DOC/OC se encontró en el suelo ASCO, que tenía el contenido del OC más bajo, pero el pH más alto. A pesar del bajo pH del suelo OVI01, el contenido de OC era relativamente soluble y su valor de DOC/OC fue el segundo entre los suelos investigados. Para el estudio del comportamiento de sorción de APCs se utilizaron cinco muestras, mientras que en el caso de PFCs se añadió el suelo DUBLIN, para disponer de un suelo con un mayor contenido de materia orgánica.

Tabla 2. Principales características de las muestras de suelo

Suelo	**Arcilla**	**Arena**	**pH**	**C (%)**	**CaCO$_3$ (%)**	**OC (%)**	**DOC (mg kg^{-1})**	$\frac{\textbf{DOC}^{a}}{\textbf{OC}}$
	(% respecto a la materia mineral)							
ASCO	17,2	18,9	8,0	6,0	38	0,2	184	0,092
ALM	10,9	56,4	5,9	1,9	2	1,6	451	0,028
GOLOSO	10,4	78,0	6,3	3,6	4	3,9	574	0,015
DELTA2	43,6	15,8	7,9	13,9	51	7,7	777	0,010
OVI01	23,6	51,7	4,6	9,5	3	9,4	5741	0,061
DUBLIN	nd	nd	5,3	nd	2	39	290	0,001

nd - no determinado

Compuestos estudiados

En este trabajo se estudiaron tres compuestos alquilfenólicos (APCs), octilfenol (OP), nonilfenol (NP) y nonilfenol-mono-etoxilado (NP_1EO) y tres compuestos perfluorados (PFCs), sulfonato de perfluorooctano (PFOS), ácido perfluorooctanoico (PFOA) y sulfonato de perfluorobutano (PFBS). Las principales propiedades fisicoquímicas de estos compuestos se muestran en la Tabla 3.

Tabla 3. Principales características de los compuestos estudiados

Familia	Compuesto	Peso molecular (g mol^{-1})	Solubilidad en agua (g L^{-1})	log K_{OW}
APCs	OP	206	12,6	4,1
	NP	220	5,4	4,5
	NP_1EO	264	3,0	4,2
PFCs	PFOS	499	0,57	5,3
	PFOA	414	3,4	4,6
	PFBS	299	46,2	2,7

Las dos familias de compuestos son surfactantes, por lo que sus propiedades dependen de las características de la parte hidrofílica y hidrofóbica. Entre los APCs, el OP es el más soluble y el menos hidrofóbico (con un menor K_{OW}), mientras que el NP es el menos soluble y más hidrofóbico. En relación con los PFCs, la solubilidad disminuye siguiendo la secuencia PFBS > PFOA > PFOS, mientras que el K_{OW} sigue la secuencia opuesta. PFBS es más soluble que PFOS y PFOA. Los valores de pK_a de los APCs son superiores a 10, por lo que estos compuestos se encontrarán en la forma neutra a los pH más habituales en matrices ambientales, mientras que los PFCs presentan valores de $pK_a < 0,14$, encontrándose en la forma aniónica.

Ensayo de lixiviación aplicado a muestras de lodos

Los ensayos de lixiviación se realizaron mediante un ensayo estándar destinado a la caracterización de residuos. Este ensayo consistió en adicionar agua doblemente desionizada a 8 g de muestra de lodo seco o la cantidad correspondiente de lodo fresco, con una relación líquido-sólido de 10 mL g^{-1} y en tubos de vidrio. Las suspensiones se agitaron a 60 rpm durante 24 h y se centrifugaron durante 30 min a 450 *g*. Los sobrenadantes resultantes se almacenaron para análisis posteriores.

Ensayos de sorción y desorción

Tres gramos de lodo o de suelo seco se pusieron en contacto, en un tubo de centrífuga, con 30 mL de una solución 0,01 mol L^{-1} de $CaCl_2$. Además, se añadieron 0,03 g de NaN_3 que actuaba como inhibidor de la biodegradación. La suspensión resultante se agitó durante 24 horas y, a continuación, se añadieron volúmenes distintos de la solución que contenía el compuesto de interés (APCs o PFCs) con el fin de cubrir un intervalo de hasta nueve concentraciones iniciales. El intervalo de concentraciones varió entre compuestos en función de sus propiedades fisicoquímicas y fue distinto para lodos (de 160 a 3920 ng mL^{-1} para PFOS, de 35 a 1040 ng mL^{-1} para PFOA y de 30 a 650 ng mL^{-1} para PFBS) y para suelos (de 0,03 a 270 µg mL^{-1} para NP, de 0,2 a 70 µg mL^{-1} para NP_1EO, de 5 a 980 ng mL^{-1} para PFOS, de 1,4 a 310 ng mL^{-1} para PFOA y de 1,3 a 150 ng mL^{-1} para PFBS). Las suspensiones se agitaron nuevamente durante 24 horas y después se centrifugaron. Los sobrenadantes se separaron del residuo sólido y se guardaron para el análisis del compuesto de interés.

Para los ensayos de desorción, algunos de los residuos de lodo o suelo resultantes de los experimentos de sorción, se secaron a 40 °C durante 48 h. Luego, se les añadieron 30 mL de $CaCl_2$ 0,01 mol L^{-1} y se agitaron durante 24 h. La suspensión resultante se centrifugó y se trató de la misma manera que en el ensayo de sorción.

Determinación de compuestos alquilfenólicos

Para realizar la cuantificación de APCs (OP, NP y NP_1EO) en las soluciones de lodo o de suelo, obtenidas a partir de la lixiviación o de los ensayos sorción y desorción, se añadieron 0,5 µg de patrón interno (NP-D8 o NP_1EO-D2) a 30 mL de la solución y se realizó una extracción líquido-líquido con 30 mL de ciclohexano. Los extractos orgánicos se evaporaron casi a sequedad en una corriente de N_2 y se reconstituyeron con acetato de etilo hasta un volumen final de 1 mL.

Las concentraciones de NP y NP_1EO se determinaron mediante cromatografía de gases acoplada a espectrometría de masas de cuadrupolo. Se utilizó una columna capilar de sílice fundida (HP 5MS) a una velocidad de flujo de 1,1 mL min^{-1} con helio como gas portador. La temperatura del inyector se fijó en 200ºC. La temperatura inicial del horno fue de 70 ° C y se mantuvo durante 1 min. A continuación, se elevó a 206°C a una velocidad de 8°C min^{-1} y, posteriormente, a 6°C min^{-1} hasta alcanzar 310°C, manteniéndose a esta temperatura durante 10 min. La determinación se realizó en modo *selected ion monitoring* (SIM) con tres ventanas de tiempo de retención. Los iones (m/z) utilizados para la cuantificación (y confirmación) de OP, NP, NP_1EO, NP-D8 y NP_1EO-D2 fueron 135 (207, 107); 135, (149, 107); 179 (193, 135); 113 (112, 228) y 181 (195), respectivamente. Los tiempos de retención fueron: 11,0; 12,4-13,2; 14,6; 15,4-16,4 y 15,4-16,7 minutos para OP, NP, NP-D8, NP_1EO y NP_1EO-D2, respectivamente. En el caso de NP y NP_1EO se realizó una cuantificación global de los distintos isómeros.

Determinación de compuestos perfluorados

Para la determinación de PFCs en las soluciones de lodo o de suelo, obtenidas a partir de los ensayos sorción y desorción, se añadió una alícuota de 0,75 mL en un vial de cromatografía, junto con 0,01 mL de la solución de estándar interno (MPFOS o MPFOA) y 0,24 mL de acetonitrilo.

Las concentraciones de PFOS, PFOA y PFBS se determinaron mediante cromatografía de líquidos (LC) acoplada a espectrometría de masas en tándem (MS/MS). El sistema analítico consistió en un Aquity UPLC conectado a un detector de triple cuadrupolo. La separación cromatográfica se realizó en una columna Eclipse XDB-C18 (150 x 2,1 mm, 5 m de tamaño de partícula) mediante gradiente de elución binario con fase móvil acetonitrilo (A) y 3 mmol L^{-1} en acetato de amonio (B). El gradiente se inició a 25% de A y 75% de B durante 1 min, aumentó a 85% de A en 5 min y después a 100% de A en 30 s, manteniéndose 30 s. Las condiciones iniciales se alcanzaron de nuevo en 1 min, y el sistema se estabilizó durante los siguientes 4 min. El análisis de los PFCs se realizó en el modo de ionización negativa por electrospray. Los compuestos se identificaron a partir de sus transiciones de cuantificación (y confirmación) características de precursor a iones producto (m/z) que fueron 299 → 80 (299 → 99); 413 → 369 (413 → 169); 417 → 372; 499 → 80 (499 → 99) y 503 → 80 (503 → 99) para PFBS, PFOA, MPFOA, PFOS y MPFOS, respectivamente. Los tiempos de retención fueron 2,7; 3,5; 3,5; 4,5; y 4,5 minutos, respectivamente.

Cuantificación de los parámetros de sorción y desorción

El coeficiente de distribución sólido-líquido de sorción, K_d (mL g^{-1}) se calculó mediante la relación entre la concentración del compuesto (APC o PFC) sorbida en la matriz (lodo o suelo), C_s (ng g^{-1}), y la concentración del compuesto en la fase acuosa en equilibrio, C_{eq} (ng mL^{-1}):

$$K_d = \frac{C_s}{C_{eq}} \qquad (1)$$

Los valores de C_{eq} se determinaron directamente para cada compuesto (por GC-MS para APCs y por LC-MS/MS para PFCs), mientras que C_s se calculó mediante la siguiente ecuación:

$$C_s = \frac{(C_{in} - C_{eq}) \cdot V}{m_s} \qquad (2)$$

donde C_{in} (ng mL^{-1}) corresponde a la concentración inicial del compuesto en la solución añadida a la muestra, V (mL) es el volumen de solución y m_s (g) se refiere a la masa seca de la muestra de lodo o suelo.

De forma similar a K_d (Ec. 1), el coeficiente de distribución sólido-líquido de desorción, $K_{d,des}$, (mL g^{-1}) se calculó de la siguiente forma:

$$K_{d,des} = \frac{C_{s,des}}{C_{eq,des}} \qquad (3)$$

donde $C_{s,des}$ (ng g^{-1}) y $C_{eq,des}$ (ng mL^{-1}) son, respectivamente, la concentración de compuesto (APC o PFC) en la fase sólida y en la fase líquida después del experimento de desorción. El valor de $C_{eq,des}$ se determinó directamente por GC-MS o LC-MS/MS, mientras que $C_{s,des}$ se calculó como la diferencia entre la concentración inicial del compuesto en el residuo resultante del experimento de sorción, $C_{in,des}$ (ng g^{-1}), y del compuesto desorbido, referido a la masa de lodo o suelo, de la forma siguiente:

$$C_{s,des} = C_{in,des} - \frac{C_{eq,des} \cdot V}{m_s} \qquad (4)$$

Finalmente, el porcentaje de desorción, D (%), se calculó a partir de la relación entre la cantidad del compuesto desorbido y la cantidad del compuesto presente en el lodo o suelo previamente al experimento de desorción, de acuerdo a la siguiente ecuación:

$$D\,(\%) = \frac{C_{eq,des} \cdot V}{C_{in,des} \cdot m_s} \cdot 100 \qquad (5)$$

Ajuste de las isotermas de sorción y desorción

Las isotermas de sorción y desorción se construyeron mediante la representación de C_s *vs.* C_{eq} y $C_{s,des}$ vs. $C_{eq,des}$ del compuesto estudiado. Las isotermas fueron ajustadas a los modelos matemáticos de Freundlich y lineal.

La isoterma de Freundlich se describe cuantitativamente a partir de la siguiente ecuación:

$$C_s = K_F \cdot (C_{eq})^N \tag{6}$$

$$C_{s,des} = K_{F,des} \cdot (C_{eq,des})^{Ndes} \tag{7}$$

donde K_F y $K_{F,des}$, cuyas unidades dependen de los valores de N, son las constantes de Freundlich del proceso correspondiente, que expresan la afinidad de un compuesto hacia un sorbente sólido dado, en la presente tesis la muestra de lodo o suelo. Por otro lado, N es un parámetro empírico que describe el grado de no linealidad de la isoterma. Valores de $N < 1$ indican una mayor afinidad del sorbente por el compuesto a bajas concentraciones que a altas, principalmente debido a la presencia de sitios de sorción de distinta naturaleza. En cambio, valores de $N > 1$, pueden indicar una sorción por debajo de la esperada a bajas concentraciones debido a una reacción competitiva en el seno de la solución (por ejemplo, formación de complejos con un ligando), o bien una interacción adicional soluto-soluto que comportaría una sorción mayor a lo esperado a altas concentraciones. Finalmente, cuando N es aproximadamente igual a 1, el modelo de Freundlich puede ser asumido como lineal, y el valor de K_F se acerca a un valor de K_d válido para todo el intervalo de concentración ensayado. En este caso, las isotermas de sorción y desorción también pueden ser ajustadas a una ecuación lineal, la cual es descrita por una pendiente constante entre C_s *vs.* C_{eq} y $C_{s,des}$ *vs.* $C_{eq,des}$ en todo el intervalo de concentración investigado. En estos casos, K_d y $K_{d,des}$ se deducen directamente de la pendiente de las isotermas.

Los parámetros de K_F y N del modelo se calcularon usando la función Solver de Microsoft Excel TM. El error estándar de los parámetros K_F y N se estimó mediante el uso de SOLVSTAT.XLS de Microsoft Excel TM.

Cálculo del parámetro K_{OC}

En la matriz de lodo o de suelo se pueden considerar dos tipos de sitios de sorción, la fracción mineral y la fracción orgánica, por lo tanto el coeficiente de distribución sólido-líquido se puede desglosar en dos valores de K_d correspondientes a cada una de las fracciones según:

$$K_d = K_{d,MIN} + K_{d,ORG} = K_{d,MIN} + K_{OC} \cdot F_{OC} \quad (8)$$

A su vez $K_{d,ORG}$ se puede desglosar en un parámetro K_{OC}, que es el coeficiente de distribución sólido-líquido del compuesto, pero referido al contenido de carbono orgánico, y el contenido de carbono orgánico por gramo de suelo (F_{OC}). La representación de K_d frente a F_{OC} permite deducir la contribución de la fracción mineral en la sorción (ordenada en el origen) y el valor de K_{OC} (pendiente de la recta).

Resultados y discusión

Interacción de compuestos alquilfenólicos en muestras de lodo de depuradora y de suelo

Lixiviación de compuestos alquilfenólicos de lodos de depuradora

En la Tabla 4 se comparan los valores obtenidos para algunos parámetros de caracterización de los lixiviados en el lodo fresco y en el lodo seco. Como puede observarse, el hecho de secar la muestra de lodo comportó un aumento en el DOC con respecto al lodo fresco, así como una disminución en el pH. Además, mientras que el carbono orgánico particulado (POC), tomado como diferencia entre el carbono orgánico total (TOC) y el DOC, fue muy elevado en el lodo fresco (> 50% del TOC), pasó a ser poco significativo en el lodo seco.

Tabla 4. Características de los lixiviados de los lodos estudiados (valor medio (desviación estándar); n = 3)

Característica	**Lodo**	**SL1**	**SL2**	**SL3**	**SL4**	**SL5**
pH	Fresco	7,8 (0,3)	7,7 (0,1)	7,6 (0,1)	7,7 (0,3)	7,6 (0,2)
	Seco	6,7 (0,1)	7,1 (0,1)	6,8 (0,1)	6,2 (0,1)	6,0 (0,1)
DOC (mg kg^{-1})	Fresco	16500 (1900)	12200 (500)	12300 (400)	16100 (2400)	35800 (900)
	Seco	35900 (60)	21300 (100)	21400 (400)	53000 (1100)	70000 (2400)
TOC^{a} (mg kg^{-1})	Fresco	53040	25300	32400	36000	80400
	Seco	32200	27400	28400	53500	78400

[a] n = 1

Estos resultados se atribuyeron a un cambio en las características de la materia orgánica como resultado del secado de la muestra, conllevando sustancias más simples y solubles, contribuyendo a la disminución del pH, y pudiendo afectar a la lixiviación de los APCs. En la figura 1 se muestran los porcentajes de lixiviación de APCs en muestras de lodo fresco y seco.

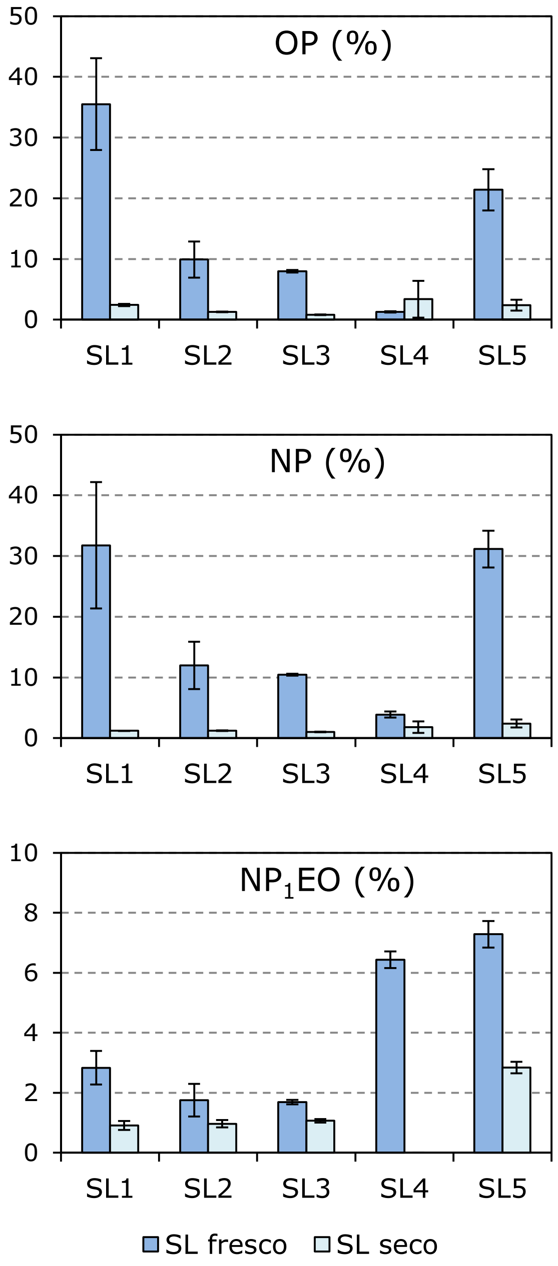


Figura 1. Lixiviación de OP, NP y NP_1EO de muestras de lodos frescos y secos

En las muestras de lodo fresco la lixiviación de OP, NP y NP_1EO varió entre 1,3 a 35%, mientras en lodo seco, la lixiviación de APCs disminuyó drásticamente a valores inferiores a 3%, y fue muy similar entre los compuestos y las muestras con distinto origen. Este comportamiento se atribuyó al hecho de que estos compuestos podían estar asociados a la materia orgánica particulada presente en el lixiviado de muestras de lodo fresco, mientras que, después del proceso de secado, los APCs permanecerían en la fase sólida del lodo, dada la casi inexistencia de materia particulada en suspensión, disminuyendo así la lixiviación.

Sorción de compuestos alquilfenólicos en suelos

Las isotermas de sorción y desorción de NP y NP_1EO en suelos fueron, en general, bastante lineales, con una $N \approx 1$ para el modelo de Freundlich. En la figura 2 se muestran las isotermas correspondientes a los dos compuestos estudiados en el suelo OVI01. La linealidad de las isotermas de sorción se explicó por los valores de C_{eq} de APCs relativamente bajos, muy por debajo de la solubilidad en agua del NP o NP_1EO, y al hecho de que al ser compuestos no polares e hidrofóbicos, presentarían básicamente una interacción con la materia orgánica por fuerzas de Van der Waals, con sitios de interacción suficientes para la sorción del compuesto. La contribución de las especies desprotonadas en la sorción fue insignificante, debido a que el pH de las muestras era muy inferior al pK_a de las sustancias, de 10,7 para el caso de NP.

La sorción de NP_1EO en dos suelos (ASCO y OVI01) resultó ser no lineal con $N>1$ ($N = 1,7$ en ASCO y $N = 1,8$ en OVI01) para el modelo de Freundlich. En este caso la no linealidad se explicó por una sorción del NP_1EO menor a la esperada a bajas concentraciones de soluto, debido a una sorción competitiva del compuesto en la materia orgánica en solución, en detrimento de la sorción en la materia orgánica de la fase sólida. Este razonamiento fue consistente con el hecho de que estos dos suelos presentaban una mayor relación DOC/OC frente al resto de suelos. Este comportamiento no se observó para NP debido a su mayor hidrofobicidad.

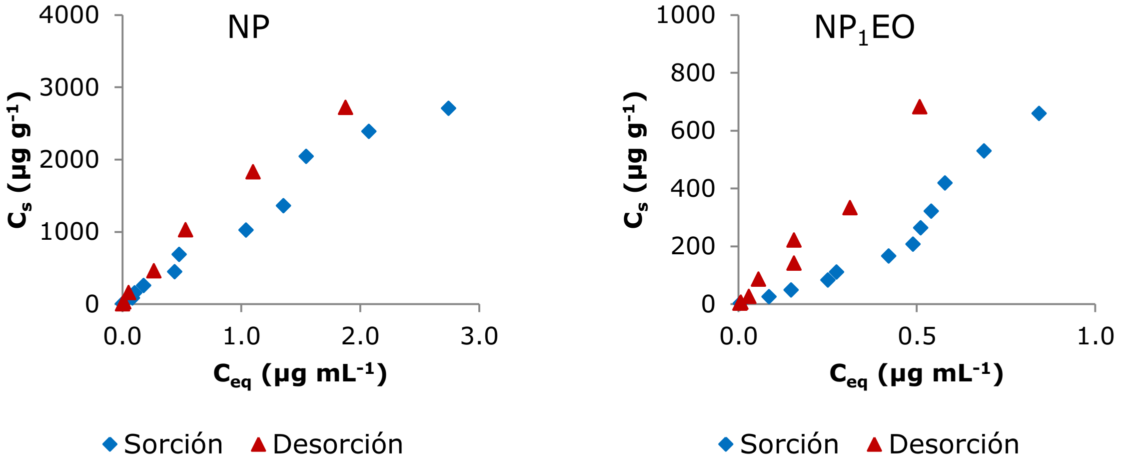


Figura 2. Isotermas de sorción y desorción de NP y NP$_1$EO en el suelo OVI01

Teniendo en cuenta que para la mayor parte de isotermas, tanto de sorción como de desorción, se obtuvieron valores de $N \approx 1$ y los valores de K_F fueron muy parecidos y estuvieron correlacionados con los de $K_{d,linear}$ para las distintas combinaciones APC-suelo, se procedió a comparar los valores de $K_{d,linear}$, de sorción y desorción, para los dos compuestos en los distintos suelos (Tabla 5). En el caso de NP$_1$EO en los suelos ASCO y OVI01 se procedió al cálculo de dos valores de $K_{d,linear}$, a bajas y a altas concentraciones de compuesto.

En la mayoría de los suelos, los valores de $K_{d,linear}$ de sorción fueron más altos para NP que para NP$_1$EO, debido a la mayor hidrofobicidad de NP. Además, los valores aumentaron con el contenido de carbono orgánico del suelo. Por lo que se refiere a la desorción, los valores de $K_{d,des}$ también aumentaron con el contenido de materia orgánica del suelo y fueron superiores a los valores de K_d de sorción, lo que demostró que el NP y el NP$_1$EO se sorben de forma irreversible en los suelos. En general, la desorción de los APCs, fue inferior a 5% para todas las combinaciones APC-suelo.

Tabla 5. Los parámetros (valor medio (desviación estándar); n = 3) del ajuste con el modelo Freundlich y lineal

APC	**Suelo**	**Sorción**		**Desorción**	
		Modelo de Freundlich	**Modelo lineal**	**Modelo de Freundlich**	**Modelo lineal**
		$\mathbf{K_F}$ (g^{1-N} mL^N g^{-1})	$\mathbf{K_{d,linear}}$ (mL g^{-1})	$\mathbf{K_{F,des}}$ (g^{1-N} mL^N g^{-1})	$\mathbf{K_{d,des}}$ (mL g^{-1})
NP	ASCO	29 (2)	24 (1)	81 (20)	130 (4)
	ALM	299 (4)	297 (7)	402 (27)	446 (18)
	GOLOSO	451 (10)	446 (10)	671 (85)	821 (25)
	DELTA2	764 (31)	795 (53)	802 (46)	862 (17)
	OVI01	1160 (67)	1059 (47)	1760 (118)	1467 (69)
NP_1EO	ASCO	60 (4)	23* (1) 79** (11)	18 (5)	24 (2)
	ALM	228 (12)	244 (12)	322 (11)	309 (9)
	GOLOSO	296 (9)	299 (9)	386 (32)	403 (20)
	DELTA2	337 (19)	371 (11)	519 (64)	470 (39)
	OVI01	929 (60)	425* (21) 1055** (142)	1470 (179)	1285 (83)

* K calculada para C < 0 5 µg mL^{-1}

La fracción de carbono orgánico del suelo (F_{OC}) fue un parámetro clave en la sorción de NP y NP_1EO en los suelos. Así, los valores de $K_{d,linear}$ estuvieron correlacionados con la fracción de carbono orgánico del suelo para NP y NP_1EO, lo que permitió deducir un valor de K_{OC} para cada compuesto a partir de la pendiente de función, siendo de 10320 mL g^{-1} para NP y de 5860 mL g^{-1} para NP_1EO. Además, el mayor valor de K_{OC} para NP se correspondía con su mayor K_{OW}.

Interacción de compuestos perfluorados con muestras de lodo de depuradora y de suelos

Sorción de los compuestos perfluorados en lodos de depuradora

Las isotermas de sorción y desorción de PFOS, PFOA y PFBS en lodos siguieron, en general, un patrón lineal para los intervalos de concentración estudiados (figura 3). El ajuste de Freundlich con valores de $N \approx 1$ para todas la combinaciones PFC-lodo, así como la buena correlación entre K_F y $K_{d,linear}$, tanto para la sorción como para la desorción confirmaron esta linealidad.

Los valores de $K_{d,linear}$ fueron bastante similares para cada uno de los compuestos en los distintos lodos, obteniéndose los más elevados para PFOS (de 104 a 218 mL g^{-1}), debido a su mayor hidrofobicidad. En el caso del PFOA, con una unidad C-F menos que le confiere una hidrofobicidad menor, la sorción fue inferior (de 28 a 50 mL g^{-1}) y el PFBS, con una cadena fluorada más corta presento los valores más bajos de $K_{d,linear}$ (de 5 a 13 mL g^{-1}).

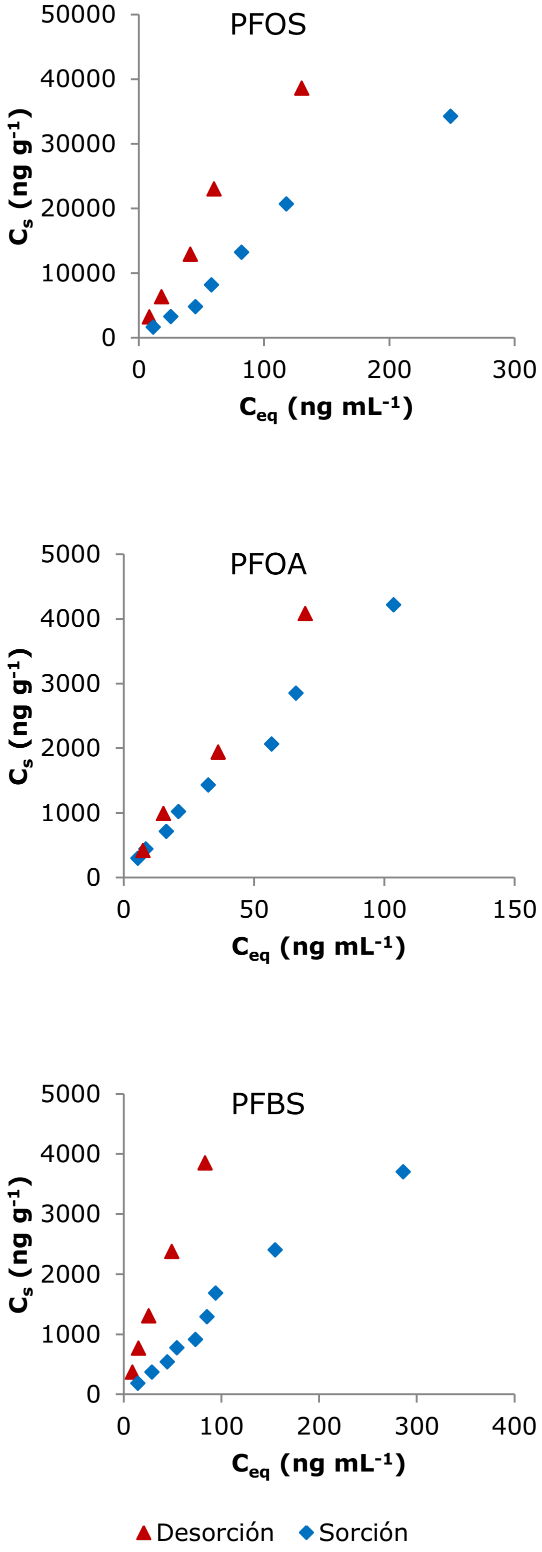


Figura 3. Sorción y desorción de PFOS, PFOA y PFBS en el lodo SL3

Teniendo en cuenta que debido a su pK_a estos compuestos se encuentran en forma aniónica al pH de los lodos, la sorción se atribuyó, por una parte, a la interacción hidrofóbica de la cadena fluorada con la materia orgánica de los lodos y, por otra, a la interacción electrostática con la superficie de los lodos a través de enlaces puente con iones Ca/Mg. Estos dos mecanismos fueron confirmados por la buena correlación entre los parámetros de sorción de PFOS y PFOA con el contenido de OM y de Ca+Mg.

Los resultados obtenidos también sugirieron que el efecto sobre la sorción de las propiedades fisicoquímicas del compuesto fue mayor que el debido a la composición y propiedades de la matriz lodo, básicamente debido a que todas las muestras tenían un contenido similar de materia orgánica. Así, se obtuvo una buena correlación entre el valor de $K_{d,linear}$ y el log K_{OW}.

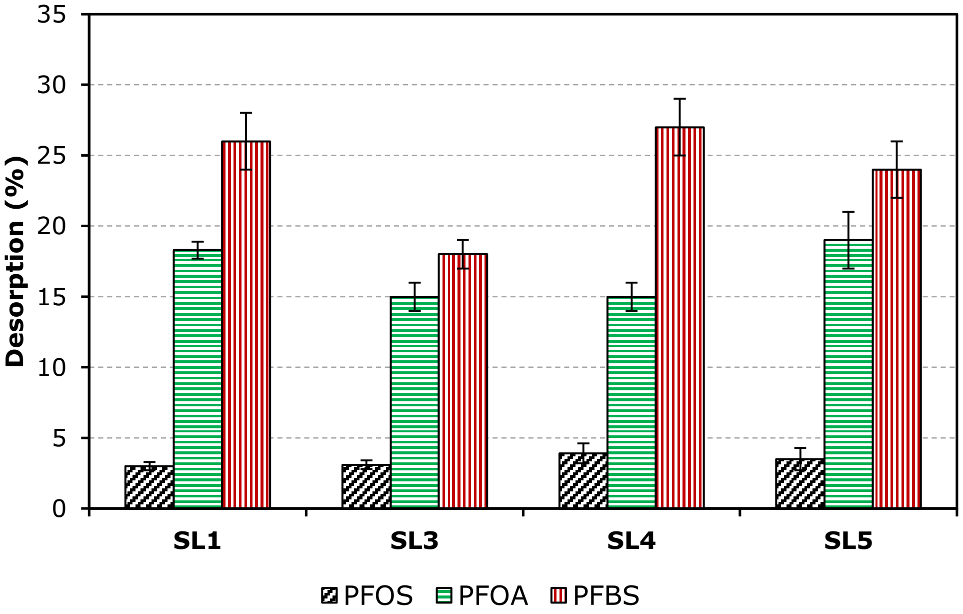


Figura 4. Porcentajes de desorción de PFOS, PFOA y PFBS en las muestras de lodos examinados

Los valores de $K_{d,des}$ mostraron la misma secuencia que los de $K_{d,lnear}$ de sorción, pero fueron sistemáticamente superiores (hasta 6 veces), lo que indicó un cierto grado de irreversibilidad en la sorción. Los porcentajes de desorción (figura 4) corroboraron este comportamiento, siendo inferiores al 4% para PFOS en todas las muestras, mientras que fueron muy superiores para PFOA y PFBS (15-19% y 18-27%, respectivamente). Por lo tanto, el PFOS mostró tanto una mayor sorción como una mayor irreversibilidad, atribuibles a su menor solubilidad en agua y mayor hidrofobicidad.

Sorción de los compuestos perfluorados en suelos

Las isotermas de sorción y desorción de PFOS, PFOA y PFBS en suelos siguieron también un patrón lineal, con valores de $N \approx 1$ para los ajustes de Freundlich en todos los casos, y una excelente correlación entre K_F y $K_{d,linear}$. Los valores de $K_{d,linear}$ aumentaron de 19 a 295 mL g^{-1} para PFOS, de 2,2 a 38 mL g^{-1} para PFOA y de 0,4 a 6,8 mL g^{-1} para PFBS, con una correlación positiva con el contenido de carbono orgánico del suelo, del mismo modo que se observó para APCs. Esta correlación indicó que el principal mecanismo de sorción de PFCs en suelos se basa, al igual que en lodos, en interacciones de Van der Waals entre la cadena hidrofóbica de C-F y la materia orgánica del suelo. Para estos compuestos los valores de K_{OC} obtenidos a partir de las correlaciones entre $K_{d,linear}$ y F_{OC}, fueron 710 (39) mL g^{-1}, 96 (7) mL g^{-1} y 16,7 (0,7) mL g^{-1} para el PFOS, PFOA y PFBS, respectivamente, siendo bastante inferiores a los valores de K_{OC} obtenidos para APCs. Mientras que los valores de $K_{d,linear}$ disminuyeron en la secuencia de PFOS > PFOA >PFBS, los porcentajes de desorción fueron inferiores a 13% para el PFOS, del 24 al 58% para el PFOA y el 32-60% para PFBS, mostrando así que las características fisicoquímicas de los PFCs, básicamente su hidrofobicidad, controlan su comportamiento de sorción en los suelos, PFOS siendo el más irreversiblemente sorbido. Así, el log K_{OC} de los tres compuestos estuvo correlacionado con el log K_{OW}, de forma análoga a lo que se había observado para APCs.

Conclusiones

Con respecto al primer objetivo de esta tesis, relacionado con la lixiviación de APCs de lodos, se pueden extraer las siguientes conclusiones:

- El secado de los lodos afectó a las propiedades de la fracción de materia orgánica y, en consecuencia, a la lixiviación de los contaminantes. El proceso de secado degradó los compuestos orgánicos en moléculas más sencillas, lo que comportó cambios en el carbónico orgánico total, un descenso en la contribución del carbono orgánico particulado en solución y un correspondiente incremento en el carbón orgánico disuelto.

- Los porcentajes de lixiviación de OP, NP y NP_1EO se situaron entre 1,3 y 35% para las muestras de lodo fresco y entre 0,8 y 3,4% para las muestras de lodo seco, lo que se atribuyó a la asociación de los APCs con la materia orgánica particulada en solución, en menor concentración en los lodos previamente secados.

- Los cambios en el patrón de lixiviación de APCs debido al secado no pueden ser extrapolados fácilmente a otras familias de contaminantes. Por ejemplo, nuestros resultados mostraron que la lixiviación de metales pesados podría aumentar. Sin embargo, se sugiere que, de forma similar a los APCs, la lixiviación de otros compuestos orgánicos hidrofóbicos podría disminuir. En consecuencia, esta práctica se recomienda como parte del pretratamiento de las muestras de lodos de depuradora antes de su adición continuada a suelos agrícolas.

En lo referente al objetivo segundo de este trabajo, relacionado con la sorción de APCs en suelos, se puede concluir que:

- Los valores del coeficiente de distribución sólido-líquido para el proceso de sorción, K_d, variaron en intervalos próximos a dos órdenes de magnitud (de 25 a 1060 mL g^{-1} para NP, y de 51 a 740 mL g^{-1} para NP_1EO). Los valores de K_d de NP fueron habitualmente superiores que los de NP_1EO, de forma similar a sus constantes de hidrofobicidad (log K_{OW} (NP) = 4,5; log K_{OW} (NP_1EO) = 4,2).

- NP y NP_1EO mostraron un comportamiento de sorción lineal, lo que se explica por una interacción hidrofóbica entre la cadena alquilo hidrofóbica del APC y la fracción orgánica de los suelos. Una excepción a este patrón fue la sorción de NP_1EO en los suelos con una mayor relación DOC/OC, para los cuales la ecuación de Freundlich mostró un $N > 1$. Esto se explica por la competencia para sorber NP_1EO entre la materia orgánica en solución y en la fase sólida del suelo, para bajas concentraciones iniciales de este compuesto.

- Se observó una correlación significativa entre K_d y el carbono orgánico de los suelos, lo que permitió derivar valores de log K_{OC} para NP (4,0) y NP_1EO (3,8), respectivamente. Estos valores fueron inferiores a los de otras familias de compuestos orgánicos, lo que sugirió que los suelos tienen una menor afinidad para los APCs.

- Las isotermas de desorción de NP y NP_1EO siguieron también un patrón lineal. Los valores del coeficiente de distribución sólido-líquido para el proceso de desorción, $K_{d,des}$, variaron dentro del intervalo 130-1470 mL g^{-1} para NP y 25-1285 mL g^{-1} para NP_1EO en los suelos examinados. Al ser mayores los valores de $K_{d,des}$ que los de K_d, se dedujo que la sorción de estos compuestos fue significativamente irreversible. Éste es un hecho positivo desde la perspectiva de adiciones continuadas de lodos a suelos agrícolas, ya que los APCs potencialmente incorporados en los suelos permanecerían sorbidos de forma irreversible, es decir, inmovilizados por la matriz de suelo.

En lo que hace referencia al tercer objetivo de esta tesis doctoral, relacionado con la sorción de PFCs en lodos de depuradora y suelos, se concluye lo siguiente:

- Tanto los modelos lineal y Freundlich ($N \approx 1$) permitieron ajustar las isotermas de sorción de PFCs en lodos. La sorción tuvo lugar debido a una interacción hidrofóbica entre la cadena perfluorada y la fracción de materia orgánica del lodo, con el rol potencial adicional de puentes iónicos de Ca/Mg para compensar las repulsiones electrostáticas entre los PFCs desprotonados y la superficie cargada negativamente de los lodos al pH de trabajo.

- Los valores de K_d de PFCs en los lodos examinados variaron en un intervalo estrecho ($K_{d,linear}$: 105 - 220 mL g^{-1} para PFOS; 30 - 50 mL g^{-1} para PFOA; y 5 - 13 mL g^{-1} para PFBS), lo que sugiere que el efecto de las propiedades de los lodos en la sorción de PFCs fue inferior al efecto del propio PFC, en parte debido al contenido similar de materia orgánica en los lodos. De acuerdo con la secuencia de log K_{OW}, la afinidad de sorción de PFCs de los lodos decreció según la siguiente secuencia: PFOS > PFOA > PFBS.

- De forma similar a lo observado en los lodos, tanto los modelos lineal y Freundlich ($N \approx 1$) describieron de forma apropiada la sorción de PFCs en suelos. Se concluye que la interacción de PFCs es también de carácter hidrofóbico, básicamente fuerzas de Van der Waals entre la cadena perfluorada y la fracción de materia orgánica en la fase sólida del suelo.

- Los valores de $K_{d,linear}$ de PFCs en los suelos investigados fueron, dependiendo del suelo, 19 - 295 mL g^{-1} para PFOS, 2,2 - 38 mL g^{-1} para PFOA, and 0,4 - 6,8 mL g^{-1} para PFBS. En consecuencia, la afinidad de sorción de los suelos para los PFCs decreció en el siguiente orden: PFOS > PFOA > PFBS, lo que confirmó que la hidrofobicidad de los PFCs gobernó su sorción en suelos.

- Los valores de K_d de PFCs correlacionaron con el contenido de carbono orgánico en suelos, lo que permitió estimar los correspondientes valores de log K_{OC}: 2,8; 2,0; y 1,2, para PFOS, PFOA y PFBS, respectivamente. Estos valores deducidos son inferiores a los de otros contaminantes orgánicos persistentes.

- Los parámetros de sorción correlacionaron con K_{OW}, lo que confirmó que la hidrofobicidad de PFOS (log K_{OW} = 5,3), PFOA (log K_{OW} = 4,6) y PFBS (log K_{OW} = 2,7) gobernó su sorción en lodos y suelos.

- Las isotermas de desorción de PFCs en lodos y suelos también siguieron un patrón lineal. Los parámetros de desorción fueron sistemáticamente superiores a los de sorción, lo que confirmó un cierto grado de irreversibilidad, que disminuyó en la secuencia: PFOS > PFOA > PFBS.

- Los porcentajes de desorción de PFOS en lodos y suelos fueron inferiores al 4% y 13%, respectivamente, lo que confirmó que este compuesto se sorbió irreversiblemente. De forma adicional, PFOA y PFBS tuvieron mayores porcentajes de desorción (hasta 27% y 60% en lodos y suelos, respectivamente), confirmando que las características fisicoquímicas de los PFCs, básicamente su hidrofobicidad, gobernaron su sorción en estas matrices ambientales.

Chapter 1. Objectives

The main objective of this doctoral thesis was to study the interaction of emergent organic pollutants, such as alkylphenolic and perfluorinated compounds (APC and PFCs, respectively), with sewage sludge and soil samples. These two families of organic compounds were selected because of their ubiquitous presence and persistence in environmental matrices caused by their physicochemical properties, and also to know the mechanisms responsible for their interaction and potential mobility in the sludge-water and soil-water systems.

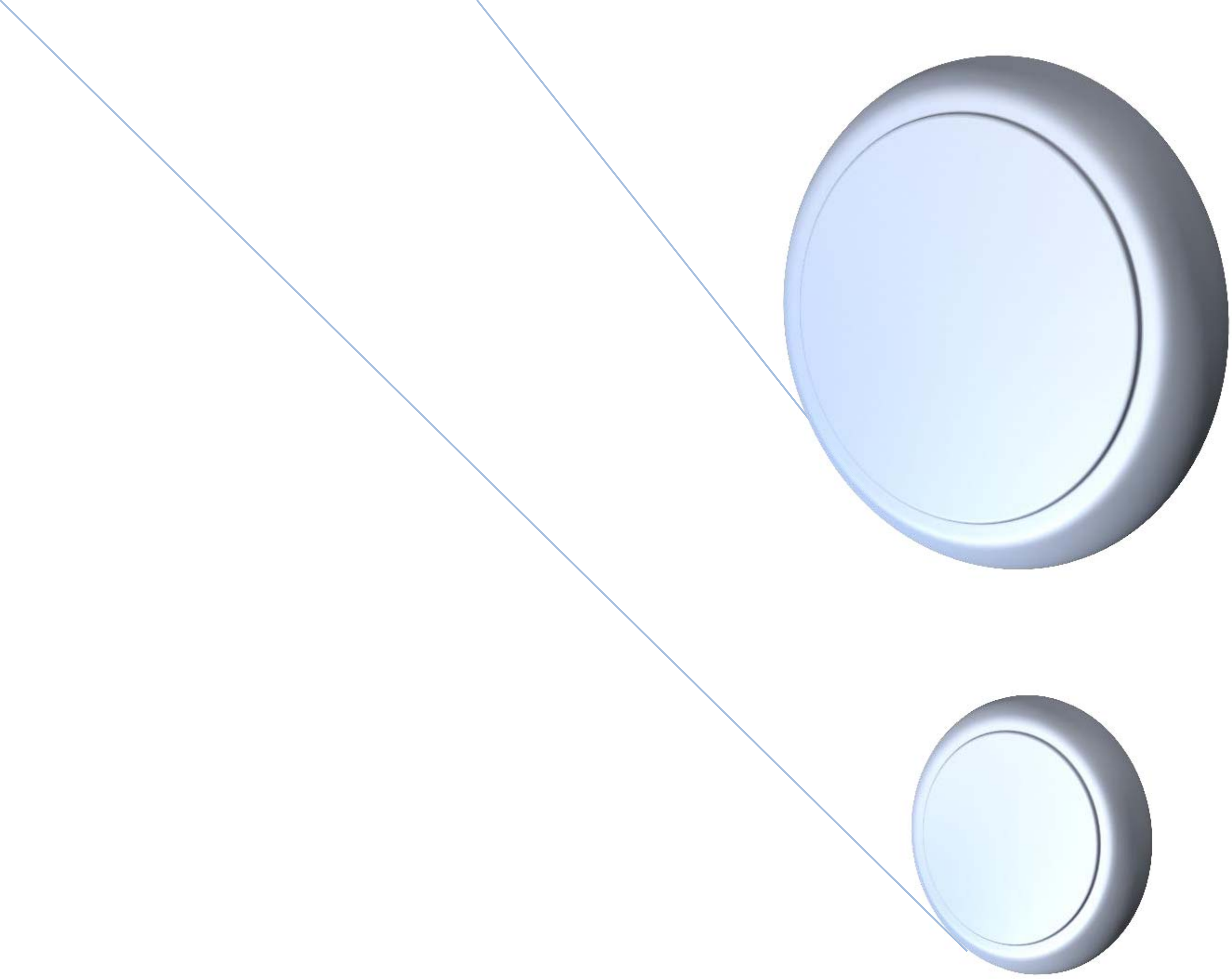
The specific objectives of this thesis may be described as follows:

1) To examine the leaching pattern of APCs from sewage sludge samples originated from different wastewater treatment plants, and to evaluate the effect of sludge drying treatment on the leachability of these pollutants.

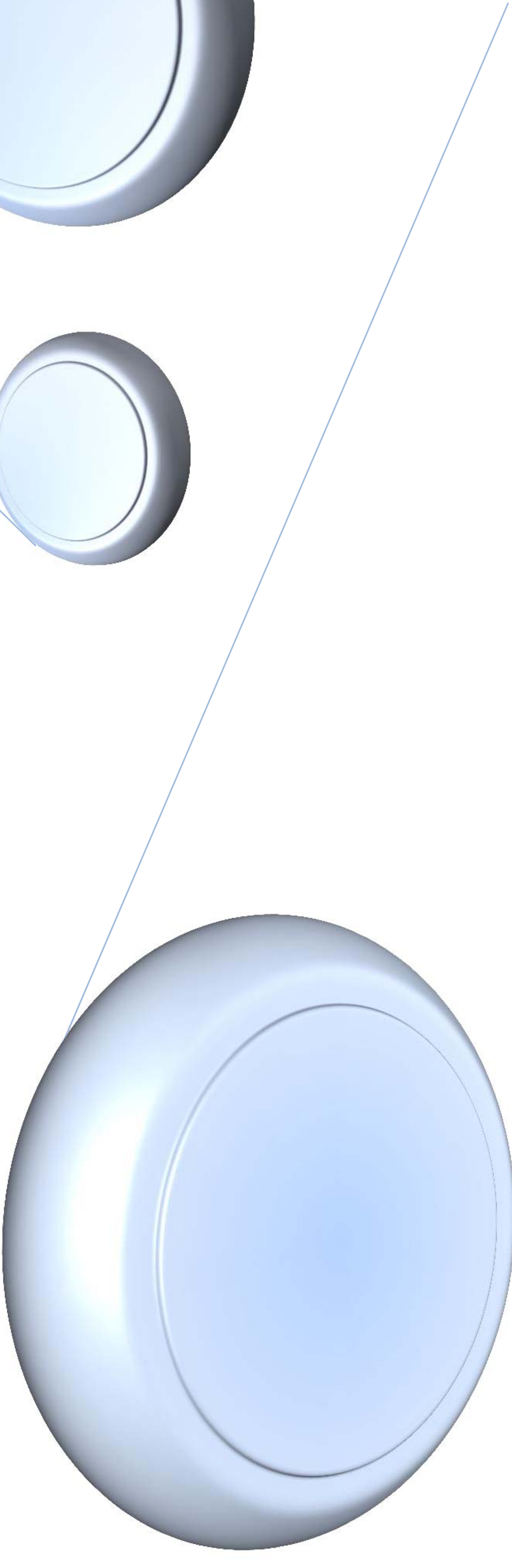
2) To study the sorption behaviour of APCs in soil samples with contrasted characteristics and to elucidate the mechanisms responsible for the APC-soil interaction.

3) To investigate the sorption behaviour of PFCs in sludge and soil samples and to determine the main physicochemical properties of the compounds and of the samples governing the PFC interaction with these sample types.

The sorption and desorption parameters obtained for APCs and PFCs, as well as the interpretation of the factors affecting these processes, will contribute to improve the prediction of the behaviour of these two families of compounds in sludge and soil samples.



Chapter 2. Introduction



2.1. Wastewater and sludge

In the last two decades, water pollution has increased to levels of concern due to the maintained increase in agricultural practices and other economic activities as well as in the urban population that eventually affects water quality. This fact has led to an increase in the number of wastewater treatment plants (WWTPs), and to the regulation of the treatment and discharge of urban wastewaters and wastewaters from industrial sectors (CEC, 1991).

Wastewater is a mixture of natural inorganic and organic materials with man-made substances (Gray, 2005). It contains everything discharged into the sewer, in addition to material washed from roads and roofs. In its broadest sense, wastewaters can be divided into domestic, industrial and urban (municipal). Domestic wastewater originates predominantly from the human metabolism and from household activities (CEC, 1991). Industrial wastewater comes from discharges from trade or industry. Urban wastewater is the mixture of domestic with industrial wastewater and/or run off rain water.

Sludge is any solid, semi-solid or liquid waste generated from domestic, industrial or municipal uses. According to the European Committee for Standardization (CEN) sludge is defined as a mixture of water and solids separated from various types of water as a result of natural or artificial processes (CEC, 2000a). Sewage sludge is the sludge obtained from urban wastewater treatment plants, whereas industrial sludge originates from the treatment of industrial wastewater (CEC, 2000a). The amount of sewage sludge, as the final product of wastewater treatment, has continuously increased, thus requiring a proper management.

2.1.1. Treatment of wastewaters

Industrial and urban wastewaters are carried through a network of collectors to WWTPs, where the main aim is to apply complementary treatment processes in order to reduce the content of inorganic and organic contaminants originally present in wastewater. The wastewater treatment process includes several steps, which depend on the WWTP. Main elements of a typical WWTP are presented in Figure 2.1.

Figure 2.1. Main elements of a typical WWTP

Each element is essential for the treatment of wastewater before it is returned to the environment or used for other purposes (ACA, 2014). In an initial stage, large solids carried by the wastewater from industrial or urban uses entering the WWTP, are separated by preliminary sedimentation using settling screens (1). The system of sand settling basin (2) is used to separate the sand carried by the effluent that is going to be treated. In the skimming tank (3) fats present in wastewater, are removed by injection of micro-bubbles that allow air to float fats.

After these treatments, wastewaters still contain suspended solids and therefore undergo a new treatment in a primary settler (4). Primary settling produces the sedimentation of floccules of organic and inorganic material which settle onto the floor of the settling tank, thus defining the primary sludge. The primary sludge is a rather unpleasant smelling thick liquid, which is highly putrescible and has the moisture content higher than 95%. This type of sludge is generally not used in agricultural applications.

In the secondary settler (5) settling is based on physicochemical processes, such as flocculation and decantation, or biological activity of the microorganisms which transform organic and inorganic matter into the more soluble forms. This activity produced secondary sludge (Figure 2.2) which undergoes further treatment processes.

Figure 2.2. Secondary sludge

2.1.2. Secondary sludge treatment processes

After treatments of wastewater, the secondary sludge is treated by a combination of processes such as thickening, pasteurisation, composting, aerobic or anaerobic digestion and dewatering.

Thickening is defined as any treatment process aiming at increasing the concentration of solids in the sludge, mainly by filtration and centrifugal acceleration (EEA, 1998). In the sludge thickener, sludge is concentrated by solid-liquid separation, then mixed and homogenised in order to reduce its volume and to be treated afterwards more efficiently. A summary of some of the possible treatment routes for thickened secondary sludge are presented in Figure 2.3.

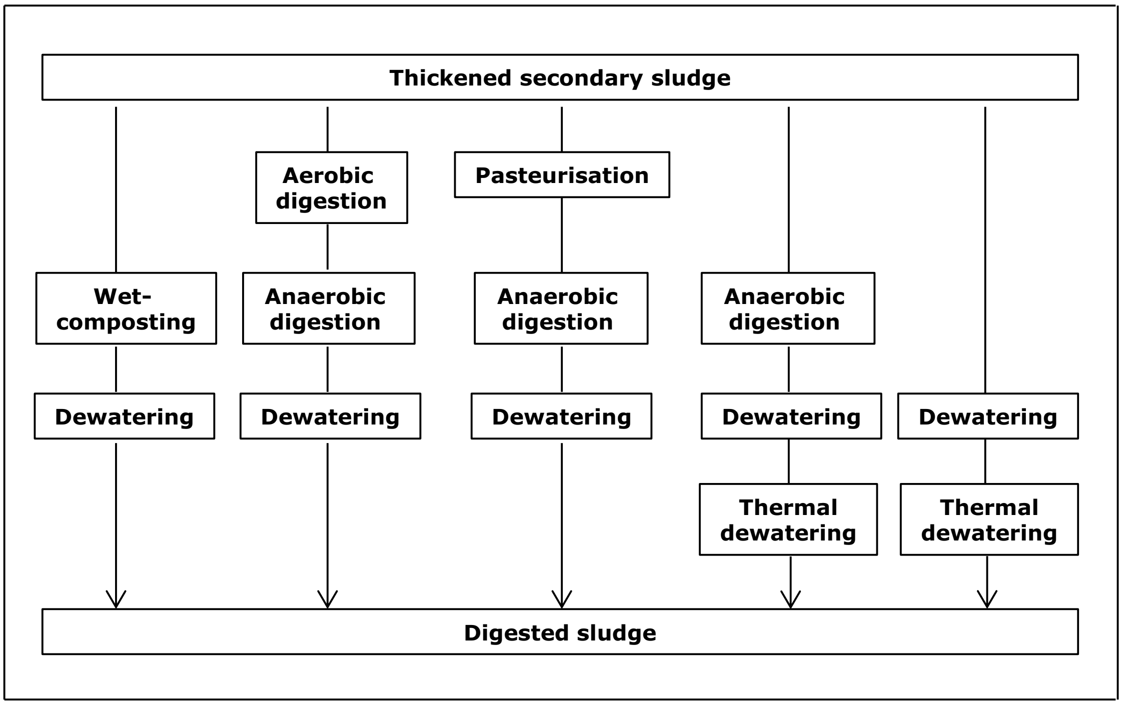


Figure 2.3. Main treatment routes for thickened secondary sludge (EEA, 1998)

Thickened secondary sludge can be digested when the fermentable part is eliminated with previous aerobic digestion or pasteurisation. The digestion is achieved through the biological activity of the same microorganisms present in the sludge under aerobic or anaerobic conditions or through the addition of chemical compounds. There is no standardised practice for sludge digestion, but the European Union (EU) defines a digested sludge as one that has undergone biological either aerobic or anaerobic, or chemical treatment with lime, or storage in a liquid form at ambient temperature.

Dewatering implies further removal of water from the thickened secondary sludge. It can be accomplished by filtration or centrifugation. Sludge dewatering and all previous processes aim at stabilizing sludge organic matter and at reducing the sludge volume to obtain a digested sludge residue easier to manipulate.

2.1.3. Sludge composition

Sludge exhibits wide variations in the properties depending on the origin of wastewater and previous treatments in WWTPs. Sludge composition is a main factor determining its quality assessment and disposal method selection.

Secondary sludge has a typical brown colour, characteristic of Fe (III) complexes. It consists of flocks composed mainly by inactive bacteria. The dry matter of secondary sludge is typically 0.2%. About 60-80% corresponds to organic solids and the rest has inorganic composition (Table 2.1).

Table 2.1. Chemical parameters of secondary and digested sludge (Qasim, 1985)

Parameter	**Secondary sludge**	**Digested sludge**
Organic solids (% dm)	60-80	30-60
Total N (% dm)	2.5-7.0	1.6-6.0
Total P (% dm)	2.0-7.0	1.4-4.0
pH	6.5-7.5	6.5-7.5
Alkalinity (mg L^{-1}, as $CaCO_3$ equivalent)	200-500	2500-3500

dm: dry matter

Major organic compounds of secondary sludge are proteins, polysaccharides and fats. Degradation products like aminoacids, monosaccharides and fatty acids are also present (Koppe and Stozek, 1999). In the inorganic fraction of secondary sludges predominate SiO_2 (30-35%), CaO (20-25%), Al_2O_3 (17-20%), P_2O_5 (12-15%) and Fe_2O_3 (6-7%), which can be in complex mineral forms. Precipitated $Ca_3(PO_4)_2$ can also be present (Hartmann, 1992). Other cations and heavy metals can be found in concentrations of mg kg^{-1} to g kg^{-1}, depending on the origin of wastewater and especially on the relevance of the fraction of industrial waste in it.

Digested sludge has a black colour and usually a dry matter of 5-20% with 30-60% of it belonging to organic solids (Table 2.1). After digestion most of the N is converted into soluble forms, mainly inorganic ammonium compounds. With respect to P, only a small fraction is likely to be in the form of organic phosphates. The mineral P (30-98% of total P) consisted mainly of compounds with Fe, Al, Ca and Mg.

Less than 10% of organic matter in digested sludge is extractable by organic solvents. The "insoluble" part consists of macromolecular structures that can be divided into lignin-derived, lipid-derived and nitrogenous compounds. Humic and fulvic acids represent in average about 17% of the organic matter of sludge (Riffaldi et al., 1982). Sludge digested under anaerobically conditions, contains relatively less alkyl-C and higher amount of oxidised forms of C (Smith et al., 2008).

Application of different digestion methods will affect the composition of sludge. For example, aerobic conditions favour the conversion of N species to the NO_3^- form, whereas after dewatering, components like soluble forms and dissolved organic matter are expected to be lost in the removed liquid phase.

2.1.4. Sewage sludge in the EU: production and management

The amount of sewage sludge derived from the WWTPs has continuously increased in the recent years within the European Union (EU). One of the factors responsible for this is the implementation of the Directives 91/271/EEC (CEC,

1991) and 98/15/EEC (CEC, 1998) concerning wastewater treatment. Concretely, the implementation of the European Directive 91/271/EEC (CEC, 1991) on urban wastewater treatment, whose main objective is to protect the environment from the adverse effects of wastewater discharges, led to the significant increase in the number of WWTPs with an ensuing production of large amounts of sewage sludge.

The total production of sewage sludge in the EU is estimated at around 102 million tons (Milieu Ltd, WRc, RPA, 2010). As shown in Figure 2.4, the amounts of sludge production differ significantly among EU member states, due to both the population as well as the sewage treatment connection rates, i.e., the percentage of national population connected to the urban WWTPs. In the previous period, the highest sludge production was in Germany, UK, France, Italy and Spain. These countries contribute to around 75% of total sludge production in the EU area.

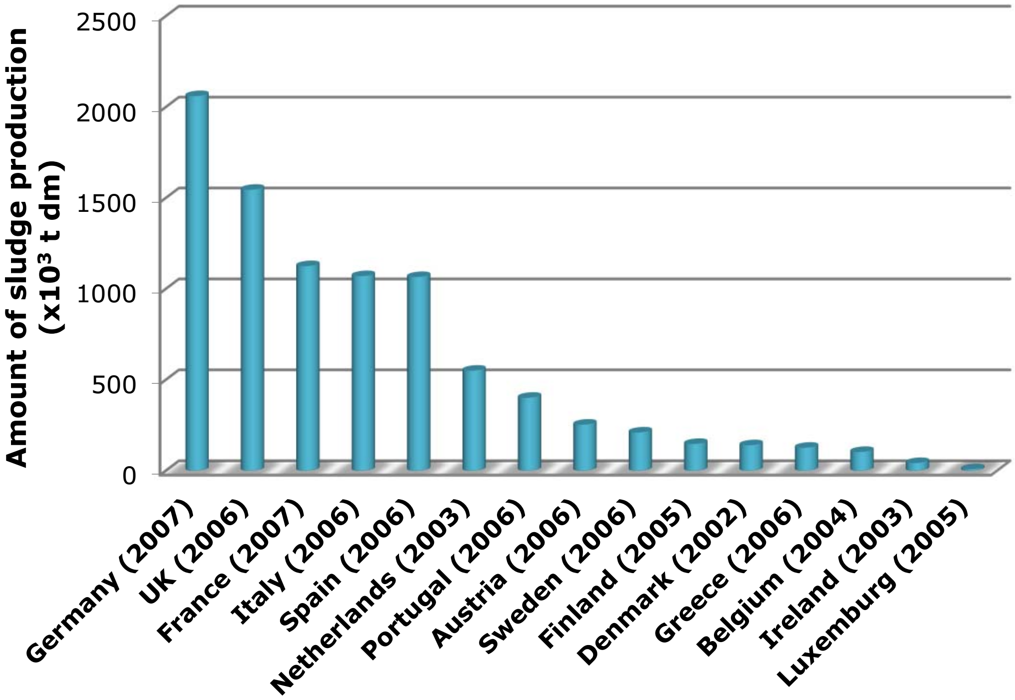


Figure 2.4. Sewage sludge production in the EU member states

The management of sewage sludge is a critical problem for environmental protection and for the administration of local communities. In order to maintain or improve the recycling of nutrients and organic matter contained in sludge, sludge management practice should intend to maximize the capacity of sludge reuse, but in an environmental protective manner.

In the EU, main disposal routes for sewage sludge are agricultural use, incineration, landfill and compost. In Figure 2.5 the average percentages of sludge disposal methods in the EU in 2005 are shown.

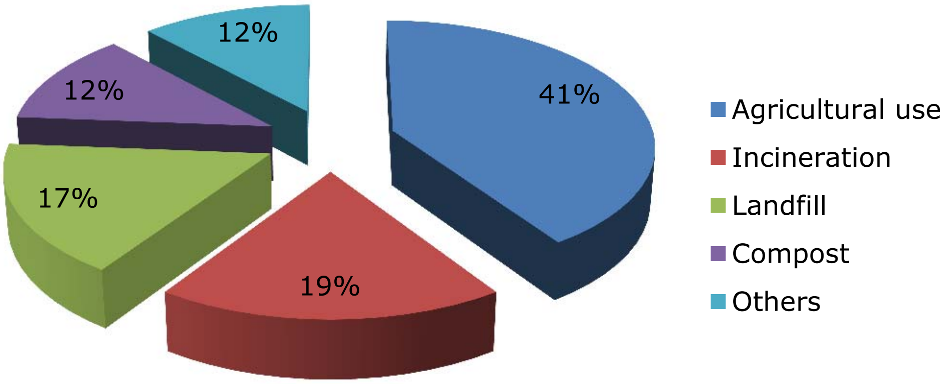


Figure 2.5. Sludge disposal methods in the EU in 2005 (Kelessidis and Stasinakis, 2012)

In general, sludge with stable organic matter is considered to be more suitable for the agricultural application and thus it could be disposed in the agricultural soils to increase either the production of the crops or/and to improve the quality of soil. Reusing sewage sludge as a soil fertilizer is an economic and environmentally acceptable method for municipal sludge management. This practice should be carried out in such a way to minimize the risk of negative effects to human health and ecosystems, the quality of groundwater, surface water and soils. The recycling of sludge to agriculture varies greatly among Member States (Milieu Ltd, WRc, RPA, 2010). In several EU countries (Denmark, France, Ireland, Spain and the UK) more than half of all sludge produced is used in agriculture. However, in a few EU Member States (Belgium and Romania) no sludge is recycled to agriculture, whereas in Finland, Netherlands, Greece and Slovenia the amount disposed in agricultural use is less than 5% of the total sludge production. It is estimated that sludge production in the EU will rise to just under 13 million tons in 2020 and the proportion of treated sludge recycled to agriculture across the EU will remain more or less the same, at 44% in 2020 (Milieu Ltd, WRc, RPA, 2010).

In some EU countries (Belgium and the Netherlands) incineration is, at present, the main alternative to spreading sludge on land, to avoid public opposition due to odour problems, among other. The use of incineration among EU countries is expected to rise slightly, from 27% in 2010, to 32% in 2020 (Milieu Ltd, WRc, RPA, 2010).

The addition of sludge to landfill was widely practiced, but due to undesirable effects, such as contamination with metals and organics or enhanced methane production and releases of greenhouse gases, it was reduced between 1992 and 2005 from 33 to 15%. In the EU Directive on landfill it is required that sludge has a minimum solids content of 35% and it also limits the amount of the biodegradable waste. Amounts of biodegradable waste should be reduced to 50% by 2015 and to 35% by 2020 (Milieu Ltd, WRc, RPA, 2010). Therefore, the use of sewage sludge for landfill will become increasingly banned within EU.

Apart from these several main disposal pathways, other sludge management actions imply that sludge can be long-term stored, reused in green areas and forestry or exported to other countries.

2.1.5. EU Directives concerning the sewage sludge application to soil

During wastewater treatment, removal of potentially hazardous substances is just partial. Within this context, some compounds tend to accumulate in the sewage sludge because of their high hydrophobic properties. Strongly hydrophobic organic contaminants can be efficiently removed during wastewater treatment and bind to the sludge solids.

In the EU Directives concerning the sewage sludge application to soil, only limit values for concentrations of heavy metals in the sludge for agricultural use, have been regulated. Nevertheless, there is a progressive effort towards including the limit values for emergent pollutants of increasing environmental interest. In 2000, the European Commission (EC) elaborated a sludge working document with the following aims:

- To reduce the quantities of potentially hazardous substances so that sewage sludge complies with the concentration limits for organic compounds as suggested for its beneficial use.

- To maximise the share of sewage sludge suitable for beneficial use as well as minimising the quantities of organic compounds released into the environment.

In this working document thresholds for heavy metals and established limit concentrations for some organic pollutants are proposed (CEC, 2000a), as shown in Table 2.2.

Table 2.2. Proposed limit values for concentrations of organic compounds in sludge for use in agriculture

Organic compound	**Limit values (mg kg^{-1} dry matter)**	
	2000	**2003**
AOX	500	500
DEHP	100	100
LAS	2600	5000
$NP+NP_1EO+NP_2EO$	50	450
PAH	6	6
PCB	0.8	0.8
PCDD/F	100	100

For instance, thresholds are suggested for: the sum of halogenated organic compounds (AOXs), di(2-ethylhexyl) phtalate (DEHP), linear alkylbenzene sulfonates (LASs), the sum of nonylphenol (NP), nonylphenol-mono-ethoxylate (NP_1EO) and nonylphenol-di-ethoxylate (NP_2EO), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs).

However, in 2003 new additional limit values were proposed for the sum of linear alkylbenzen sulfonates (5000 mg kg^{-1}) and for the sum of nonylphenol, nonylphenol-mono-ethoxylate and nonylphenol-di-ethoxylate (450 mg kg^{-1}) (Salado et al., 2008).

2.2. Incorporation of organic contaminants in soil

Soil is a complex system that can incorporate organic contaminants through several routes, such as industrial activities, agricultural chemicals or inadequate disposal of wastes, such as sewage sludge. As previously explained, sludges originated from WWTPs can be used as a soil fertilizer and therefore, the contaminants originally present in sludges can be leached from sludges to soils after sludge application.

In order to understand chemical interactions that may occur between organic contaminants and soils, it is fundamental to know the chemistry of soil components, as the chemical reactions that contaminants may undergo in the soil environment highly affect their subsequent mobility and bioavailability.

2.2.1. Soil: definition and main phases

Soil is the weathered and fragmented outer layer of the earth's terrestrial surface. It is formed after the disintegration and decomposition of rocks by physical and chemical processes, and it is influenced by the activity and accumulated residues of microscopic and macroscopic plants and animals (ISO, 2005). Soil is an open, multicomponent, biogeochemical and dynamic system consisting of three main phases: solid, liquid and gas phase (Figure 2.6) (Sposito, 2008).

In a typical soil for plant growth, the solid phase represents about 50% of the total soil volume and it consisted on a mineral fraction and an organic matter fraction. Generally, a mineral fraction is predominant compared to the soil organic matter. The gas phase of soil comprises about 20-25% and liquid phase typically makes up remaining 25-30% of soil (Sparks, 2003). Distribution of all three phases can change depending on the location, weather conditions and other factors.

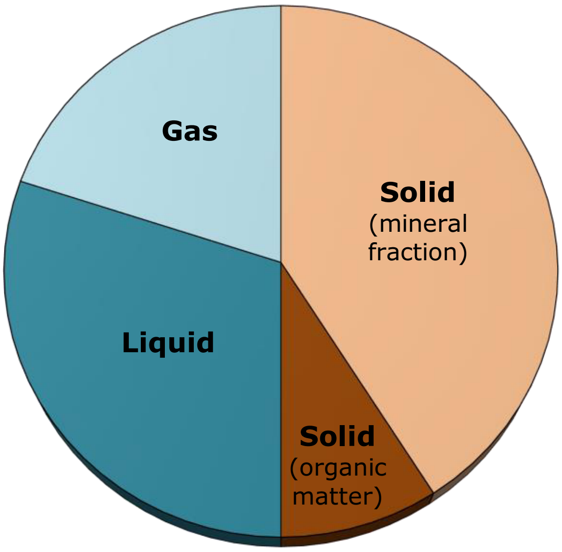


Figure 2.6. Main soil phases

2.2.2. Mineral fraction of soil

The mineral fraction of soil is mainly composed by O, Si, Al and several other elements in minor proportion, such as Fe, Ca and K. This fraction of soil includes primary and secondary minerals, which are characterized by different particle size. Primary minerals occur in the sand (2 mm - 50 µm - diameter) and in the silt fractions of the mineral matter (50 - 2 µm particle diameter), such as silicates (quartz) and metal oxides (hematite). Secondary minerals can be mainly found in the clay fraction (< 2 μm in size) (Moore and Reynolds, 1989), such as hydrated aluminosilicates with a laminar structure (phyllosilicates). Depending on the sand, slit and clay percentages, soil texture can be established according to the texture triangle of the United States Department of Agriculture (USDA) (Figure 2.7).

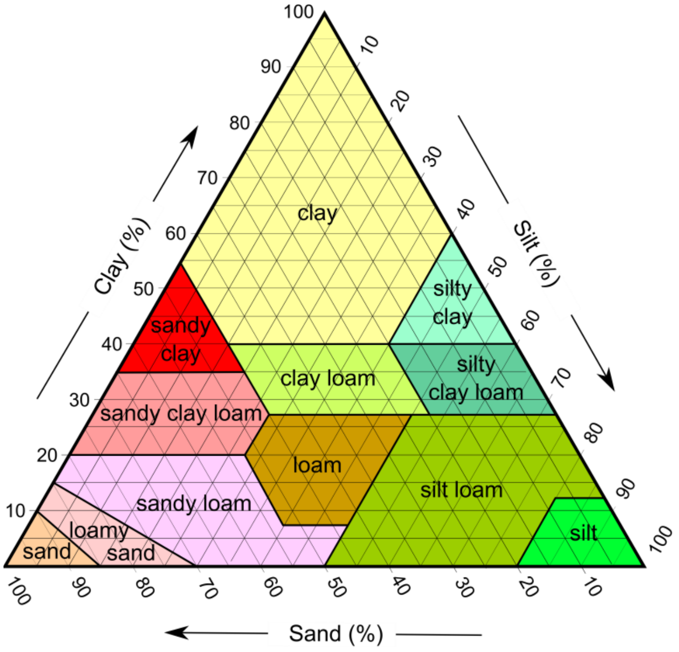


Figure 2.7. Soil texture

In general, the most important minerals of the soil mineral fraction from the point of view of interaction are:

- Metal oxides, consisting in oxides, oxyhydroxides and hydroxides of Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{4+} and Al^{3+}, which can have complex mineralogy with crystalline or amorphous phases. Interaction capacity of metal oxides is associated with the permanent charges generated by isomorphic substitutions either by cationic or surface oxidation processes.

- Carbonates. The predominant forms are calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), which possess a high cation exchange capacity through the ionic bond between Ca^{2+} and Mg^{2+} with CO_3^{2-}.

- Phyllosilicates. They have a laminar structure based on two types of layers: tetrahedral layers, composed by tetrahedrons with silicon as a central atom and four shared oxygen atoms; and octahedral layers, composed by octahedrons containing aluminium as a central atom and six shared oxygen atoms. Two main groups of phyllosilicates can be described, depending on the combination of these two types of layers: 1:1 phyllosilicates (one tetrahedral layer and one octahedral layer) and 2:1 phyllosilicates (one unit of octahedral layer between two units of tetrahedral layers). Kaolinites are the most typical minerals of 1:1 type, whereas illites and smectites are the most usual among 2:1 phyllosilicates. The isomorphic substitution of Si^{4+} by Al^{3+} in the tetrahedral layers and of Al^{3+} by Fe^{2+} or Mg^{2+} in the octahedral layers generates permanent negative charges, mainly on the surface of the tetrahedral layers, which may be compensated by the sorption of cations.

The mineral fraction of soil is expected to have a minor role in the incorporation of organic contaminants in soils. Natural clay minerals contain exchangeable metal ions which make their surfaces hydrophilic and hence they are ineffective in sorbing non-ionic organic compounds from aqueous solutions. However, some clays, essentially phyllosilicates, can be responsible for the sorption of polar or cationic organic compounds (Calvet, 1989). In addition, the metal ions, as constitutive units of crystalline and amorphous minerals, such as Ca^{2+} and Mg^{2+} can be involved in the electrostatic interactions with deprotonated organic compounds.

2.2.3. Organic matter of soil

Organic matter (OM) of soil or humus is any material produced originally by living organisms after decomposition process. Soil OM includes the total organic compounds in soils, excluding plant and animal tissues, their products and the soil biomass (Sparks, 2003).

Soil OM consists of humic and non-humic substances. The non-humic substances include carbohydrates, proteins, peptides, aminoacids, fats, waxes and low molecular weight acids. These compounds are attacked easily by soil microorganisms and persist in a soil for a short time. Humic substances are a general category of naturally occurring, biogenic, heterogeneous organic substances being yellow to black in colour, with a high molecular weight (Aiken et al., 1985). Depending on their water solubility, humic substances can be divided into fulvic acids, humic acids and humin. While the humic acids are soluble in acids and fulvic acids are soluble in both acids and basic media, humin is an insoluble fraction of soil OM. Important hydrophobic sites of the humic substances include lipids, waxes, resins and aliphatic side chains.

The organic fraction of soil is expected to play a main role in the incorporation of organic contaminants in soils. The sorption capacity of this soil fraction is mainly based on numerous functional groups of various organic compounds, mainly humic substances in soils, with contrasting hydrophilic and hydrophobic character (Sparks, 2003).

Organic matter content in soils can be also expressed as a content of the organic carbon (OC) in soils. Mineral soils may contain from trace to 30% of organic matter (18% of organic carbon), whereas organic soils have more than 30% of organic matter (FAO, 2001). Even in soils with a relatively low OM content, the reactivity of soil OM is high and it has a pronounced effect on soil chemical reactions.

2.2.4. Soil solution

Soil solution or liquid phase of soil is the medium composed by water present in the pores of the solid matrix, available compounds and ions in soil solution, and suspended matter (Sparks, 2003). Compounds and ions in the soil solution can be free or forming complexes with dissolved organic or inorganic components of soil. Movement of compounds and ions to the soil solution can also occur after drying and evaporation process.

Among soil organic compounds, soluble fulvic and humic acids can be released from the solid phase to the liquid phase, constituting part of the dissolved organic carbon (DOC) of soil, and interact with different organic contaminants. Soils may have a significant content of DOC, of both hydrophilic and hydrophobic character (Matějková and Šimon, 2012). Hydrophilic fraction of DOC contains simple organic acids, polyhydroxyl phenols, carbohydrates, aminoacids and aminosugars, while hydrophobic fractions comprise phenols, hydrocarbons, fatty acids and nucleic acids (Gigliotti et al., 2002). The hydrophobic fraction of DOC preferentially interacts with hydrophobic organic contaminants, whereas ionic species may interact with the hydrophilic DOC fraction.

2.3. Interaction between organic compounds and solid environmental matrices

Not only the total concentration, but also the distribution of organic compounds between the solid and liquid phase of the environmental matrices is important to know. In general, distribution of organic compounds between the solid matrix and its liquid phase in equilibrium depends on both physical and chemical reactions which may occur between them.

There are several equilibrium reactions of the compound in the liquid-solid interface in an environmental matrix. The liquid phase is a medium from which the compound can be sorbed at the solid phase, whereas the sorbed compound can be desorbed into the liquid phase. Furthermore, if the liquid phase is oversaturated with a compound, the compound can precipitate and incorporate into the solid phase. On the other hand, if the solution becomes unsaturated with a compound present in the solid phase, the compound can be dissolved. Free compound can be transported depending on its physicochemical properties, such as solubility, polarity and hydrophobicity. Finally, through evaporation and drying, the movement of a compound to liquid phase can also occur.

There are a number of complex chemical reactions that can occur between organic compounds and the solid phase of an environmental matrix. Main reactions are ion exchange and protonation, hydrogen bonding (an electrostatic interaction between positively charged H^+ ion and a negatively charged ion, such as O^{2-}), Van der Waals forces and ligand exchange (an organic functional group such as a carboxyl or hydroxyl group displaces an inorganic hydroxyl or water molecule of a metal ion at the surface of a sorbent mineral such as oxide, resulting in an inner-sphere complex) (Sparks, 2003).

The overall interaction will depend on the combination of many factors. On the one hand, the composition of the solid phase (basically, mineral or organic) and, therefore, the number and type of interaction sites present, as well as, the state of these sites (protonated or deprotonated) depending on the pH of the media. The composition of the liquid phase is also important, e.g. the presence of DOC can compete with the solid phase for the sorption of the organic compound or the presence of metal ions may facilitate the interaction of the organic compound with deprotonated sites, through bridge bonds. Finally, the physicochemical characteristics of the target compound, such as solubility or polarity, affects the partitioning of the compound between the solid and liquid phases. These physicochemical properties depend also on the conditions of the media, such as pH, that influences the ionic state of the functional groups of the target organic compound as a function of their pK_a values.

2.3.1. Sorption and sorption reversibility

Sorption is a general term which includes all processes related to the incorporation of a compound into a solid matrix (sorbent), including adsorption, surface precipitation and polymerization. Adsorption can be defined as the accumulation of the compound at the interface between the matrix surface and the liquid phase (Sparks, 2003). Adsorption includes the removal of the compound (solute) from the matrix solution and is responsible for the retention of the compound by the solid phase of the sorbent (Essington, 2004). In addition to adsorption, the compound can be absorbed into sorbent OM. During absorption, compound migrates into the sorbent structure, thus this retention of compound is not strictly a surface process.

Sorption reversibility represents the fraction of the sorbed compound that can participate in the reversible equilibrium between the solid matrix and its liquid phase (Figure 2.8). This process determines the release of sorbed compounds from the sludge or soil to the water solution (Stumm, 1992). Apparent irreversible incorporation of compound leads to a commonly observed characteristic of sorption processes: desorption hysteresis. The hysteresis is the increase in the sorption of a compound when equilibrium is approached from desorption direction, i.e. when the sorption of compound is irreversible (Essington, 2004).

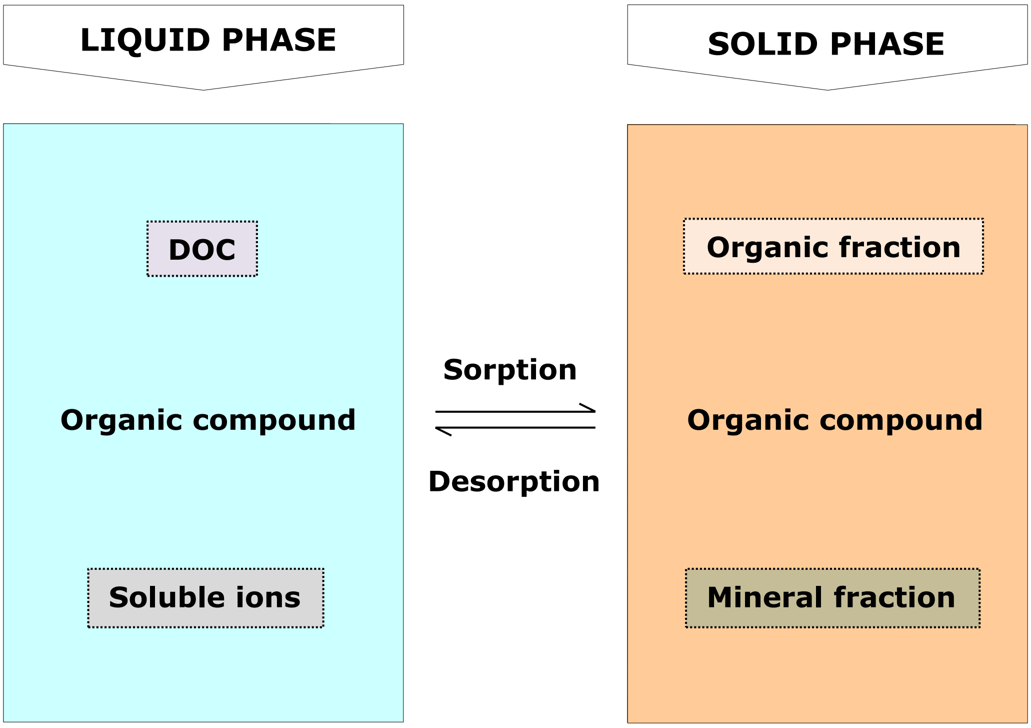


Figure 2.8. Distribution of organic compound in the solid/liquid phase in the environmental sample

Because the sorption process often restricts compound mobility and bioavailability, a mechanism is needed to quantitatively indicate the extent of the sorption process. The quantitative measures of sorption and its reversibility could then provide information on the potential mobility of a compound as a function of the soil and the chemical conditions in the soil. A general approach which provides a quantitative measure of compound sorption by soil relies on determining the distribution of compound between the solid and solution phases at equilibrium.

2.3.2 Sorption and desorption parameters

Sorption is often described by the solid-liquid distribution coefficient, K_d (mL g^{-1}), which is the ratio between the concentration of the compound sorbed in the solid phase (C_s) and its concentration in the liquid phase (C_{eq}) at equilibrium:

$$K_d = \frac{C_s}{C_{eq}} \tag{2.1}$$

The distribution coefficient describes the affinity of compounds to be sorbed to the sorbent. Thus, to evaluate environmental fate of a given compound, the quantification of K_d in sludge and soil is of crucial importance.

Similarly, desorption solid-liquid distribution coefficient, $K_{d,des}$ (mL g^{-1}), is the ratio between the concentration of compound in the solid phase and the concentration of the desorbed compound in the liquid phase when desorption equilibrium is reached:

$$K_{d,des} = \frac{C_{s,des}}{C_{eq,des}} \tag{2.2}$$

Hence, for higher K_d and/or $K_{d,des}$ values, the compound will be more sorbed to the sorbent. In the case of sorption hysteresis, the desorption coefficient, $K_{d,des}$ is higher than the respective sorption coefficient, K_d (Essington, 2004).

Apart from the sorption and desorption solid-liquid distribution coefficients, sorption and its reversibility can be expressed as the sorption percentage, S (%) and desorption yield, D (%), respectively. Sorption percentage is defined as the ratio between the amount of compound sorbed in the matrix with respect to its amount initially added in the solution, whereas desorption yield represents the ratio between the desorbed concentration of compound in the solution and the initial concentration of compound in the solid phase.,

2.3.3. Laboratory tests to study sorption behaviour of compounds

Sorption and desorption solid-liquid distribution coefficients of a compound, K_d and $K_{d,des}$ can be estimated *in situ* or from laboratory experiments. *In situ* long-term monitoring requires very specific equipment for measurements and it implies direct measurement of a compound in the field. In the experimental conditions, K_d and $K_{d,des}$ can be deduced from the known concentrations of compound in solid and liquid phase (Eqs. 1 and 2) obtained from the laboratory tests. Batch and flow-through (in column) are the most common setups at laboratory level to obtain K_d and $K_{d,des}$ values (Sposito, 2008).

In the simplest, traditional batch technique, a certain amount of a sorbent (m_s) is placed into a series of vessels, such as centrifuge tubes with a known volume (V) of solution (Figure 2.9).

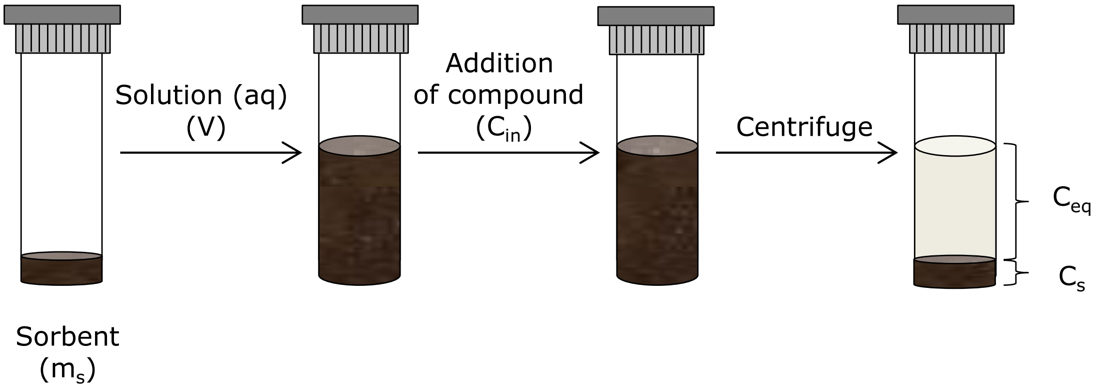


Figure 2.9. A simple scheme of sorption test

Sorption tests are usually performed in 0.01 M $CaCl_2$ solution as liquid phase (OECD, 2000). A soil/liquid (S/L) ratio may vary from 1:1 up to 1:100 and selection of the appropriate S/L ratio depends on the compound and its relative degree of sorption. The most common is S/L ratio of 1:10. After a pre-equilibration time with the solution, a known concentration of compound (C_{in}) is added to the suspension. After an adequate equilibration time the liquid and solid phases are separated by centrifugation and/or filtration to obtain clear supernatant for analysis. The concentration of compound in the solution is measured (C_{eq}), and the concentration in the solid phase (C_s) deduced as follows:

$$C_s = \frac{(C_{in} - C_{eq}) \cdot V}{m_s} \tag{2.3}$$

Desorption test is carried out with a dry solid residue after sorption test (Figure 2.10) in order to evaluate the sorption reversibility of the compound.

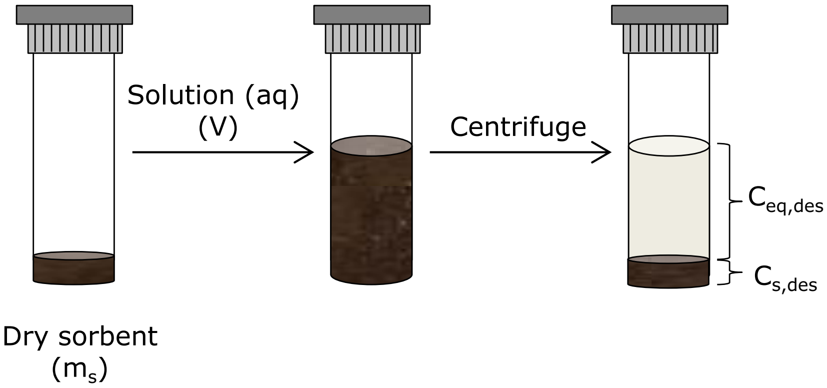


Figure 2.10. A simple scheme of desorption test

The same solvent as in sorption experiment is added to the dry sorbent residue (in the same S/L ratio as in previous sorption test) and after equilibration time, the liquid and solid phases are separated by centrifugation and/or filtration to obtain clear supernatant for analysis. The concentration of compound in the solution is measured ($C_{eq,des}$), and the concentration in the solid phase ($C_{s,des}$) deduced as follows:

$$C_{s,des} = C_{in} - \frac{C_{eq,des} \cdot V}{m_s} \tag{2.4}$$

2.3.4. Sorption isotherms

The use of sorption isotherms is the most applied approach to describe the sorption mechanism of compound in solid-liquid systems. A sorption isotherm describes the relation between the changes in the sorbed concentration of an analyte (C_s) with changes in its equilibrium concentration in the liquid phase (C_{eq}). Additional plotting of K_d *vs.* C_s can facilitate the selection of the most appropriate isotherm which can describe the sorption or desorption mechanism (Hinz, 2001). Based on their initial slopes and curvatures, the sorption isotherms are classified in four main types: H-type (high affinity), C-type (linear or constant partition), S-type (sigmoidal shape) and L-type (Langmuir) isotherm classes (Figure 2.11). To account for plateaus, points of inflection and maximum values, these classes can be further distinguished between subgroups (Hinz, 2001). The K_d coefficient is often used to transform sorption data to confirm different classes and subgroups of sorption isotherms (Hinz, 2001).

H-type isotherms have a convex shape and the slopes of this type of isotherms reach high values at low concentrations (Figure 2.11). This indicates that the sorption of H isotherms increases with decreasing concentration. This behaviour is mainly attributed to the presence of sites of different affinity, as confirmed by the K_d *vs.* C_s plot, with a high decrease of K_d values at low concentrations, and a lower decrease at high concentrations.

C-type isotherms are defined by a constant sorption affinity, expressed as a straight line in C_s *vs.* C_{eq} plots and a constant value of K_d *vs.* C_s. This behaviour is consistent with conditions in which the sufficient number of sorption sites is constantly occupied by the solute molecules with the same affinity throughout the concentration range. Many organic substances follow this type of isotherm (Hinz, 2001).

L-type isotherm is characterised by an initial region, which is convex to the concentration axis. The L-shaped isotherm is characterised by a decreasing slope as concentration increases. Differently from the H-type isotherm, this decrease in sorption is not attributed to sites of different affinity, but to a progressive saturation of sorption sites of the same nature. This behaviour is confirmed by a constant decrease of K_d *vs.* C_s. The slope of L-isotherms should be constant when the concentration approaches zero.

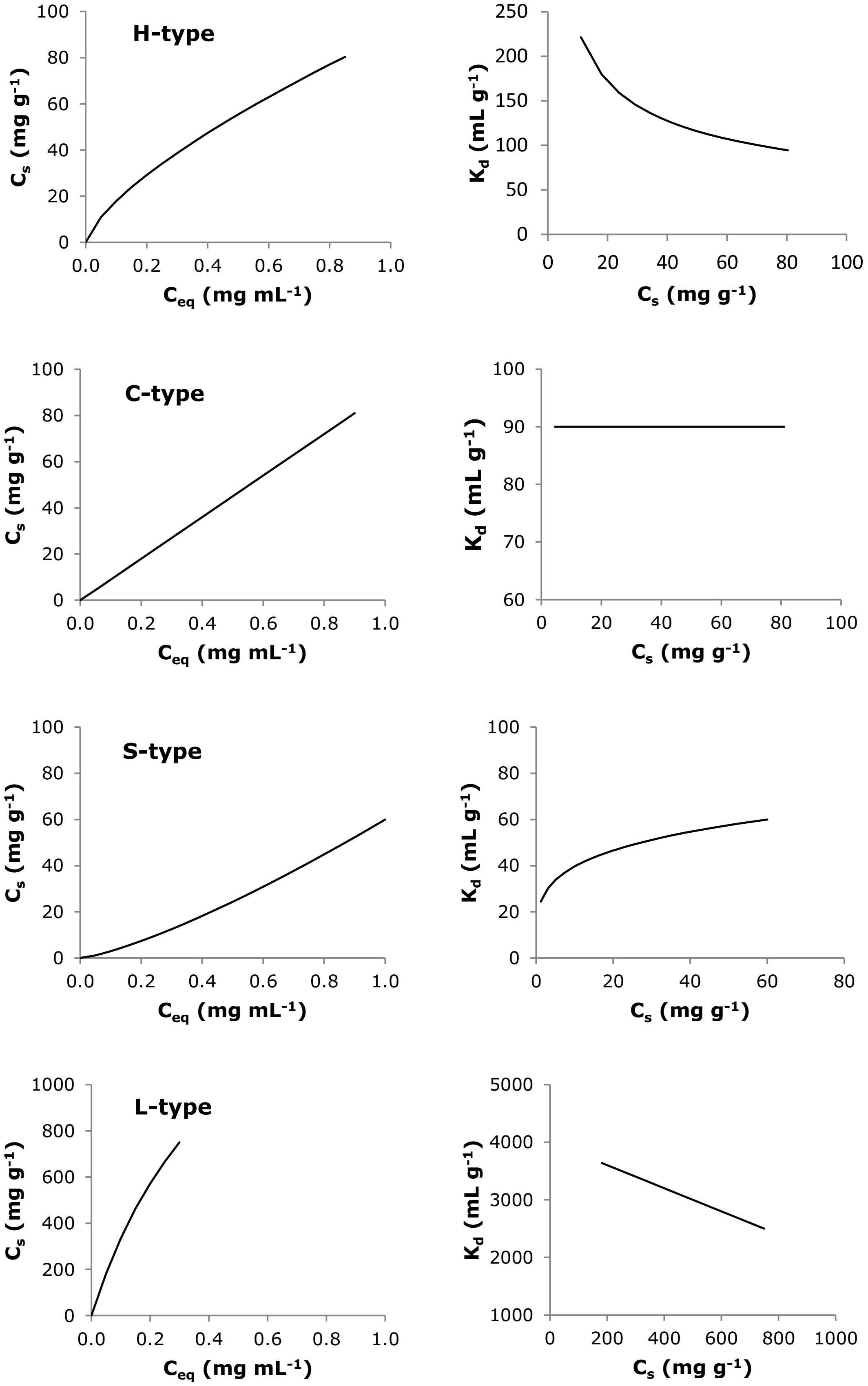


Figure 2.11. General types of sorption isotherms (Hinz, 2001)

S-type isotherms have, in general, a concave shape at low concentrations. Isotherms of the S-type have two main causes. First, the sorption of the solute may be inhibited by a competing reaction within the solution, such as a complexation reaction with a ligand. Second, solute-solute attractive forces at the surface may cause cooperative sorption which leads to the S-shape (Hinz, 2001). Literature shows that this second mechanism for S-isotherms is observed frequently for the organic molecules sorbed on some clays (Calvet, 1989). In general, this type of isotherm is less frequent than H- C- and L- types (Hinz, 2001).

2.3.5. Fitting of sorption isotherms

The sorption isotherms can be fitted my mathematical criteria which include curvature (convex or concave), slope at low concentration, asymptotic behaviour at high solute concentration in liquid or solid phase, and the number of plateaus and inflection points (Hinz, 2001). Each type of sorption isotherm can be fitted by different model equations.

Mathematical criteria to define L-type isotherms are based on sorption behaviour at low concentrations. The most common model which can describe L-type isotherms is the Langmuir equation, which can be expressed as:

$$C_S = \frac{b \cdot K_L \cdot C_{eq}}{1 + (K_L \cdot C_{eq})} \qquad (2.5)$$

where b (μg g^{-1}) is the maximum amount of compound that can be sorbed and K_L (mL g^{-1}) is the Langmuir constant related to the site sorption energy. In the development of this equation most of the assumptions, such as sorption occurs on planar surfaces with fixed number of sites that are identical or the energy is the same for all sites and independent on surface coverage, are not valid for the heterogeneous surfaces in sorbents (Sparks, 2003).

Sorption isotherms can also be fitted by the widely used empirical Freundlich model, which considers heterogeneous surface sorption sites with varying affinity for a given compound. It can be expressed by the following equation:

$$C_S = K_F \cdot C_{eq}^N \tag{2.6}$$

where K_F ($\mu g^{(1-N)}$ mL^N g^{-1}) is the the Freundlich constant and N (dimensionless) is the Freundlich parameter which describes the site heterogeneity. If the Freundlich exponent $N \approx 1$, the Freundlich sorption constant will be equal to K_d (Eq. 1) and plots C_s *vs.* C_{eq} will be linear, thus describing a linear sorption model and assimilating to a C-type isotherm. If the exponents are not equal to 1, sorption isotherms will be non-linear and K_d will vary along the isotherms. This model can fit also H-type isotherms, giving $N < 1$, or S-type isotherms, for which $N > 1$ values are obtained.

C-type isotherms exhibit constant affinity for a wide range of concentrations, implying that the K_d is constant and can be deduced directly from the slope of the linear regression of sorption isotherm. At trace concentrations many solute-sorbent systems behave this way.

More complex models have been developed for explaining some particular solute-sorbent interactions of higher complexity. Thus, sorption isotherms of certain organic compounds can be a "mixture" of basic isotherms, indicating that the sorption mechanism do not correspond strictly to the basic models. As an example of a particular S-type isotherm, Figure 2.12 shows a two-step isotherm consisting of a mixture of linear and non-linear sorption isotherms.

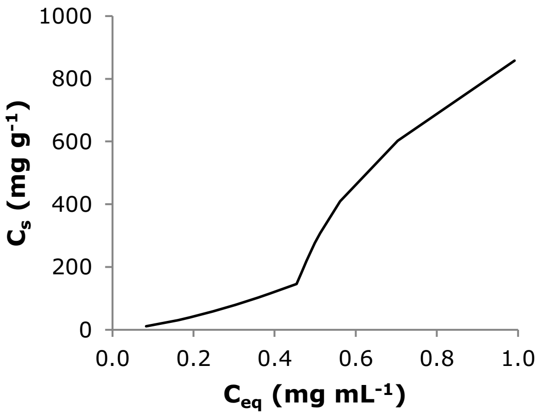


Figure 2.12. S-type of sorption isotherm with two C_s *vs.* C_{eq} slopes

For this specific case, the relation C_s *vs.* C_{eq} can be described by a two-step sorption isotherm curve that can be fitted by the combined Langmuir-Freundlich (L-F) model, after applying the following equation derived by Czinkota et al. (2002):

$$C_S = \sum_{i=1}^{s} \frac{q_{Ti}K_i(C_{eq} - b_i + |C_{eq} - b_i|)^{n_i}}{2^{n_i} + K_i\,(C_{eq} - b_i + |C_{eq} - b_i|)^{n_i}} \tag{2.7}$$

where *s* is the number of steps of isotherm and each step depends on four parameters: q_{Ti} (μg g^{-1}) - the sorption capacity of the solute, i.e., specific sorbed amount of the solute; K_i ((mL $g^{-1})^{n_i}$) - the equilibrium constant, b_i (μg mL^{-1}) - the critical concentration limit of the solute and n_i - the average degree of association in solid phase assigned to the i-th step of the curve (Czinkota et al., 2002).

2.3.6. Sorption of organic compounds by the organic matter

In a simplistic approach, a sorbent such as soil may be considered as a mixture of two main site pools, the organic and mineral fractions. As suggested by Karickhoff (1981), an organic compound can be sorbed at both site pools of sorbent and therefore, its sorbed concentration can be expressed as follows:

$$C_s = C_{s,MIN} + C_{s,ORG} \tag{2.8}$$

In this expression, $C_{s,MIN}$ and $C_{s,ORG}$ correspond to the concentrations of the compound sorbed into the mineral fraction and into the organic fraction of the environmental matrix, respectively. By simple dividing of Eq. 2.8 with the concentration of compound in liquid phase at equilibrium (C_{eq}), the following expression can be obtained:

$$K_d = K_{d,MIN} + K_{d,ORG} = K_{d,MIN} + K_{OC} \cdot F_{OC} \tag{2.9}$$

$K_{d,MIN}$ value corresponds to the sorption distribution coefficient of a compound in the absence of sorbent organic matter, whereas $K_{d.ORG}$ is the sorption distribution coefficient of a compound between organic matter and liquid phase. Thus, K_{OC} is the sorption coefficient normalized to organic carbon of sorbent and F_{OC} represents the gram of organic carbon content per gram of sorbent.

The correlation between the distribution coefficient of the organic compound and organic matter fraction of sorbent can be graphically presented as in the Figure 2.13.

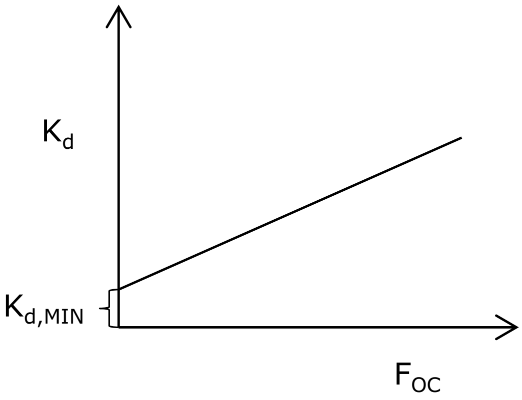


Figure 2.13. Correlation between the distribution coefficient (K_d) of organic compound and the fraction of soil organic carbon (F_{OC})

From the correlation it is possible to deduce if the mineral fraction plays a role in the sorption of the organic compound. An intercept close to zero indicates that there is non-significant interaction between the compound and the mineral fraction. On the other hand an increase of K_d as a function of F_{oc} denotes sorption of the compound in the organic matter, and the slope of the correlation, corresponding to K_{oc} value, indicates the significance of this interaction.

Additionally, depending on the characteristics of the compound, it is possible that the interaction with organic matter depends mainly on the physicochemical properties of the compound, such as octanol-water partition coefficient (K_{OW}) and solubility. K_{OW} is the ratio between the concentrations of compound in n-octanol and in water, at equilibrium. Partition coefficients between n-octanol and water can be determined using the OECD method (OECD, 1981). K_{OW} is a dimensionless value and may vary over a wide range (10^{-3} - 10^{7}) for different families of compounds. High K_{OW} ($> 10^{4}$) values are characteristic of more hydrophobic molecules, which tend to be associated with solid organic matter, whereas more hydrophilic molecules have low K_{OW} ($< 10^4$) values.

Linear correlations have been found between log K_{OC} and log K_{OW} or log Solubility and for different families of organic compounds, with the empirical coefficients having different values (Karickhoff, 1981; Chiou et al., 1983):

$$\log K_{OC} = a \cdot \log K_{OW} + b \qquad (2.10)$$

$$\log K_{OC} = m \cdot \log \text{Solubility} + n \qquad (2.11)$$

The advantage of using this type of correlations is the possibility to estimate the log K_{OC} value of a new compound of the same family for which parameters *a* and *b* or *m* and *n* have been established. This permits to estimate the K_d for specific compound by knowing the fraction of organic matter (or organic carbon) in the target matrix and thus predict the environmental distribution of the compound.

2.4. Organic compounds studied in this work

2.4.1. Alkylphenolic compounds

Alkylphenolic compounds (APCs) are characterised by the presence of a hydrophobic chain of variable length, from C-1 to C-16, the most common being C-8 and C-9, and a hydrophilic group (phenol- or phenol-ethoxylate) attached to the chain. These functional groups provide them properties of surfactants and hence they have industrial and technological applications such as cleaning products, household detergents, emulsifiers in pesticide formulations, etc. (Ahel and Giger, 1985a).

APCs may induce toxic effects because they possess chemical structure similar to estrogenic hormones, and hence can compete with regular hormones by binding to characteristic hormone receptors in the cells. APCs can mimic biochemical activities of the estrogenic hormones, even at concentrations several orders of magnitude below natural hormones (Warhurst, 1995). Hence, they show estrogenic activity and consequently are known as endocrine disrupting chemicals (EDCs) (Routledge and Sumpter, 1996).

In this thesis, several compounds of the APCs family were studied.

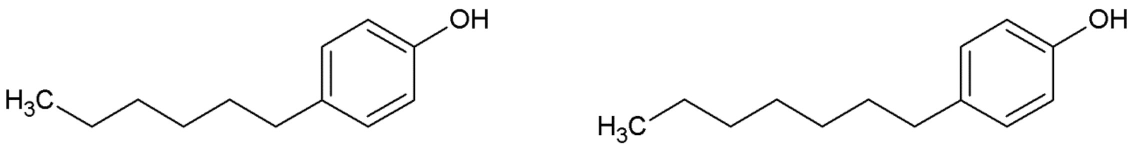
2.4.1.1. Structure, origin and use

Depending on the structure of the hydrophilic part of the molecule, APCs can be divided into two main groups: alkylphenols (APs) and alkylphenol ethoxylates (APEOs) (Figure 2.14). Alkylphenols are phenolic compounds with one or more alkyl groups attached to the phenolic ring, whereas APEOs have one or more ethoxy units, attached to the aromatic ring. The position of the hydroxyl group in the aromatic ring, relative to the position of the alkyl chain, may vary but in the environment the most ubiquitous isomers are with *para* positions. All commercial products are usually mixtures of compounds with the isomeric structures based on branched alkyl chains.

APCs are widely used as intermediate chemicals in cleaning and industrial processes. The spectrum of their applications ranges from dispersing agents in paper and pulp production to emulsifying agents in latex paints and pesticide formulations, flotation agents, industrial cleaners, cold cleaners for cars and household cleaners (Thiele et al., 1997). The majority of APCs are used as aqueous solutions and hence they are discharged into municipal and industrial WWTPs.

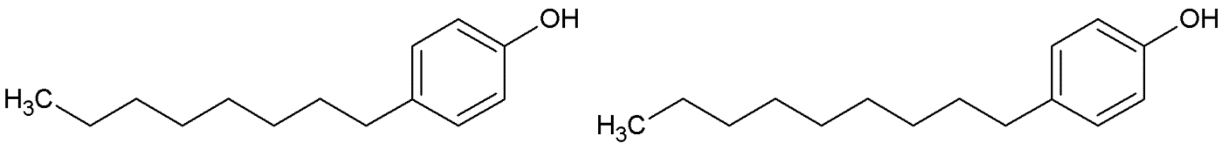
2-sec-butylphenol

4-tert-butylphenol



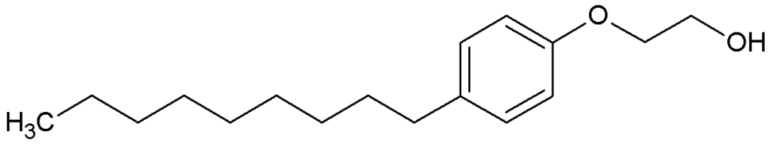
hexylphenol

heptylphenol

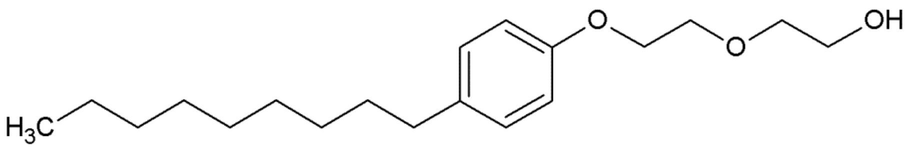


octylphenol

nonylphenol



nonylphenol-di-ethoxylate



nonylphenol-di-ethoxylate

Figure 2.14. Chemical structure of main APCs

APs are synthesized through alkylation of phenols and the most representative are nonylphenols (NPs) and octylphenols (OPs) that comprise hydrophobic alkyl group (i.e., nonyl- or octyl-, respectively) and a hydrophilic, phenol group. NPs are released in the environment as a mixture of 18 isomers with branched nonyl- groups, including the well-known linear isomer nonylphenol (NP). One of the most soluble APs is 4-t-octylphenol (4-t-OP), which was included in the list of priority hazardous substances because of its toxicity and persistence (CEC, 2000b).

Alkylphenol ethoxylates are compounds in which the phenol group is ethoxylated with one or more ethoxyl groups. APEOs are compounds with both a hydrophilic part (the ethoxyl oligomer head) and a hydrophobic part (the alkyl chain group). These structural characteristics give the compounds their typical properties of surfactants.

Most commercial APEOs are in fact mixtures of compounds for which the number of C atoms in the alkyl chain is fixed, but the structure of the alkyl chain and the number of ethoxy oligomers varies. Nonylphenol-ethoxylates with one (NP_1EO) and two ethoxy groups (NP_2EO) are the most abundant compounds. NP_1EO and NP_2EO usually show the highest concentration in aquatic environments where they can persist for decades because of their relatively low biodegradability in sediments (Shang and Macdonald, 1999).

Nonylphenol-ethoxylates (NPEOs) are the most widely used polyethoxylates of alkylphenolic compounds and they contribute to almost 80% of the total APCs. NPEOs are used as surface active agents in cleaning products, cosmetics and hygienic products, and in emulsifications of paints and pesticides.

2.4.1.2. Physicochemical properties

The main physicochemical properties of several compounds from the family of APCs are given in Table 2.3. APCs are generally solids with the exception of the dodecylphenol, which is a liquid.

Table 2.3. Main physicochemical properties of the APCs

APC	CAS	Mw (g mol^{-1})	Water solubility (mg L^{-1})	Log K_{ow}
2-*s*-butylphenol	89-72-5	150	1.7x10^{1}	3.3
4-*t*-butylphenol	98-54-4	150	8x10^{2}	3.3
hexylphenol	2446-69-7	178	29.7	4.5
heptylphenol	72624-02-3	192	12.2	4.5
4-*t*-octylphenol	140-66-9	206	12.6[b]	4.1[c]
octylphenol	1806-26-4	206	3.1	5.5
nonylphenol	104-40-5	220	5.4[b]	4.5[c]
dodecylphenol	210555-94-5	262	2.1	7.1
nonylphenol-mono-ethoxylate	104-35-8	264	3.0[b]	4.2[c]
nonylphenol-di-ethoxylate	20427-84-3	308	3.4[b]	4.2[c]

[a] - (USEPA, 2009)

[b] - (Ahel and Giger, 1993a)

[c] - (Ahel and Giger, 1993b)

The solubility of APCs depends on the characteristics of their hydrophilic and hydrophobic groups. For non-ionic surfactants, such as APCs, solubility in water obviously depends on the number of polar groups forming the hydrophilic part of the molecule as well as on the non-linearity of the alkyl chain, so that the branched isomers are more water soluble. The solubility of APEOs in water is based on the hydration of ether functional groups through hydrogen bonds and if the number of ethoxylate groups increase, their solubility also increases. Lower APEOs oligomers, with less than five ethoxylate groups, such as NP$_1$EO, NP$_2$EO are usually described as water insoluble or lipohilic, whereas higher oligomers are water soluble or hydrophilic. APs are more water soluble than the APEOs with the same chain length, except for octylphenol and dodecylphenol, which have lower water solubility of 3.1 and 2.1 mg L^{-1}, respectively. Water solubility of 4-t-octylphenol is significantly greater than the corresponding NP and its ethoxylate derivatives, indicating a predominant influence of the hydrophobic chain length on solubility. Shortening the alkyl chain for one methylene group has a considerably larger effect on the solubility increase which shows the predominant influence of the hydrophobic group on the solubility of these compounds (Ahel and Giger, 1993a).

The partition of APCs between n-octanol and water is presented by the log K_{OW} values, which ranged from 3.3 to 7.1 (Table 2.3). The log K_{OW} of NP_1EO and NP_2EO, are equal showing that the difference of one ethoxy group has a negligible impact on the lipophilicity of APEO (Ahel and Giger, 1993b). However, log K_{OW} values obtained for these compounds are 0.3 units lower than the analogous partition coefficient of NP (Ahel and Giger, 1993a). The pK_a values of APCs are higher than 10, (for ex. for NP $pK_a = 10.7$), which means that these compounds are present in the neutral form in the environmental pH solutions (pH 5-8).

2.4.1.3. Determination techniques

APCs are found in environmental samples as complex mixtures consisting of various homologues and isomers of different alkyl chain length and structure. Hence, chromatographic separation of APCs is the optimal technique for their separation and analysis. In that sense, liquid chromatography (LC) or gas chromatography (GC) coupled to mass spectrometry (MS) are widely used as suitable methods for the APCs analysis, although GC-MS has become the dominant technique for the determination of the APCs in environmental matrices (Thiele et al., 1997).

2.4.1.4. Environmental distribution

Surfactants such as APEOs are very common water pollutants, in part because they are primarily used in aqueous solutions which are later introduced into the environment via wastewater discharge. In WWTPs a complex biodegradation mechanism of APEOs, characterised by the formation of several metabolic products was established (Rudlng and Solyom, 1974). APEOs can be degraded under aerobic or anaerobic conditions, forming carboxylated (APECs) or ethoxylated (APEOs) oligomers with shorter hydrophilic group (Figure 2.15).

APECs and APEOs with short hydrophilic group (n=0,1) are further degraded in anaerobically digested sewage sludge to APs, predominantly NP, more lipophilic compound resistant to further microbial degradation with a tendency to sorb to the sludge (Ahel et al., 1994). Under anaerobic conditions NP will degrade slowly, and thus is expected to be in high concentration in this type of sludge (Gruttner et al., 1997).

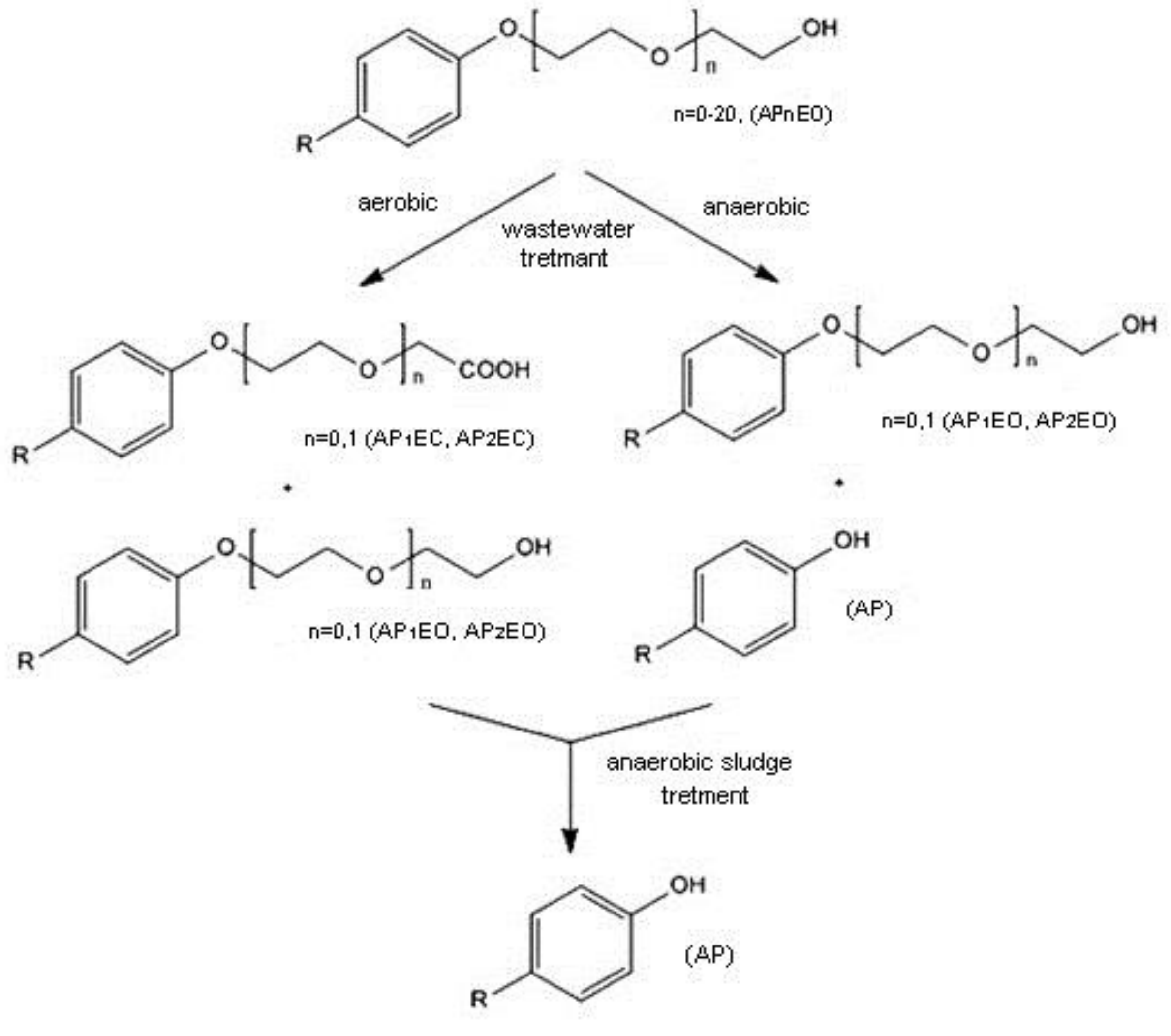


Figure 2.15. Degradation of APEOs to APs under aerobic and anaerobic conditions (adopted from Ahel et al., 1994)

APCs are not produced naturally. Their presence in the environment is solely a consequence of anthropogenic activity. APCs enter the environment, primarily, via industrial and municipal WWTP effluents, but also to direct discharge such as additive in pesticide application. APCs were detected in ambient air, water, soil, sediments and biota (Ying et al., 2002).

Among all APCs, NP, OP, NP_1EO and NP_2EO have been detected in effluents of many WWTPs worldwide (Table 2.4). NP was found in the highest concentration of 343 µg L^{-1} in northeast Spain. In the USA, NP was detected in effluent samples collected from Michigan WWTPs in concentrations ranging from 0.02 to 37 µg L^{-1} (Snyder et al., 1999). The concentrations of 4-t-OP ranged from 0.02 to 0.67 µg L^{-1} in the USA WWTPs. APEOs were detected only in the effluents of WWTPs in Japan and Switzerland (Table 2.4).

Table 2.4. APCs concentration in effluents of different WWTPs

Country	**APC concentration range (µg L^{-1})**				**Reference**
	NP	**OP**	**NP_1EO**	**NP_2EO**	
Canada	0.8-15	0.2-1.7	-	-	Lee and Peart, 1995
Germany	0.03-0.08	0.002-0.07	-	-	Kuch and Ballschmiter, 2001
Japan	0.1-1.2	0.02-0.48	0.2-3.0	-	Isobe et al., 2001
Spain	6-343	-	-	-	Sole et al., 2000
Switzerland	8	-	49	44	Ahel and Giger, 1985b
USA	0.02-37	0.002-0.67	-	-	Snyder et al., 1999

The occurrence of APCs has been widely reported in surface waters (rivers, lakes and coastal waters) around the world (Ying et al., 2002). The highest reported levels were of 644 µg L^{-1} for NP, of 20 µg L^{-1} for NP_1EO and NP_2EO and 0.47 µg L^{-1} for OP. The reported levels of these substances in sediments were much higher than the surface waters. Their highest concentrations varied between 13700 µg

kg^{-1} for NP and 670 μg kg^{-1} for OP. In Canada the NP, OP, NP_1EO and NP_2EO were found at μg g^{-1} dry weight concentrations in sediments.

Dried sludge samples from European WWTPs have yielded concentrations of 0.47-4000 μg kg^{-1} for NP, 0.66-680 μg kg^{-1} for NP_1EO and 0.04-280 μg kg^{-1} for NP_2EO (Ying et al., 2002). Sewage sludge in the region of northeast Spain contained between 100 and 500 mg kg^{-1} of NP, while river sediments in the upstream of WWTPs contained between 50 and 200 mg kg^{-1} of NP, indicating that NP has been widely dispersed in this area (Sole et al., 2000). The levels of NP in the sludge of Canada were found from 137 to 470 μg g^{-1}.

2.4.2. Perfluorinated compounds

Perfluorinated compounds (PFCs) are organic compounds in which all carbon-hydrogen bonds are replaced with carbon-fluorine (C-F) bonds. Apart from a hydrophobic fluorinated carbon chain, PFCs contain a polar, hydrophilic head attached to one end of the carbon chain, which provides them the unique chemical properties as surfactants. PFCs have surface active properties and are excellent surface protectors due to their properties of repelling both water and oil.

Due to the high energy of C-F bonds, these compounds are extremely stable on hydrolysis, photolysis and microbial degradation (Giesy and Kannan, 2001). PFCs are resistant to breakdown, and may be accumulated in the environment attached to proteins and biomagnified through the food chain. In recent years, interest for PFCs has increased due to their widespread environmental distribution, in addition to their toxic properties, such as endocrine disrupting activity and carcinogenesis (Kannan, 2013).

PFCs are widely used in several industrial applications, such as stain and water resistant textiles, food packaging, fire-extinguishing formulations, pesticides, paints, personal care products and surfactant agents (Giesy and Kannan, 2001; Paul et al., 2009; Wang et al., 2009; Wang et al., 2010).

In this thesis, several compounds of the PFCs family were studied.

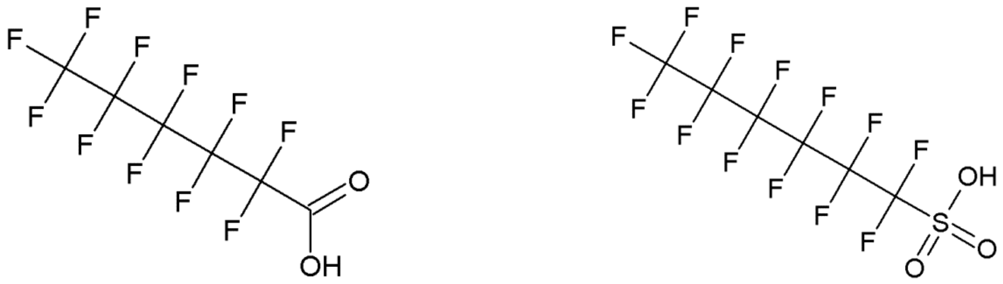
2.4.2.1. Structure, origin and use

PFCS are characterized by a fully fluorinated hydrophobic linear alkyl chain of varying length (typically C-4 to C-16), attached to different hydrophilic groups, such as sulfonate or carboxylate (Figure 2.16). Perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS) and perfluorooctane sulfonate (PFOS) belong to the sulfonate family as they have $R\text{-}SO_3$ group attached to the end of the C-F chain. Perfluorononanoic acid (PFNA) and perfluorooctanoic acid (PFOA) belong to the group of perfluorinated acid compounds with a carboxylic acid group (R-COOH).

Among all PFCs, PFOS and PFOA are the terminal degradation end-products, and hence the compounds that have been mostly detected in the environmental samples as they often occur at higher concentrations. PFOS has a fluorinated eight C-chain to which a sulfonate group is attached. PFOS was the key ingredient of a fabric protector made by the company 3M, and of numerous stain repellents. PFOS has drawn considerable scientific and public interest because of its toxic properties. Once released PFOS behaves very differently from what is usually expected for the persistent organic pollutants (POPs). Namely, POPs are organic substances which persist in the environment, can undergo long distance transportation, are bioaccumulative and pose a risk of causing adverse effects to animals and human health (Wang et al., 2009). Although PFOS and its salts have different intrinsic properties than other POPs, such as surface activity, water solubility, bioaccumulation potential, the Stockholm convention considered PFOS and its salts to meet criteria of a POP, and hence they are added to the list of persistent organic pollutants in the Annex B (UN, 2009). This means that production and use of chemicals containing PFOS should be minimized.

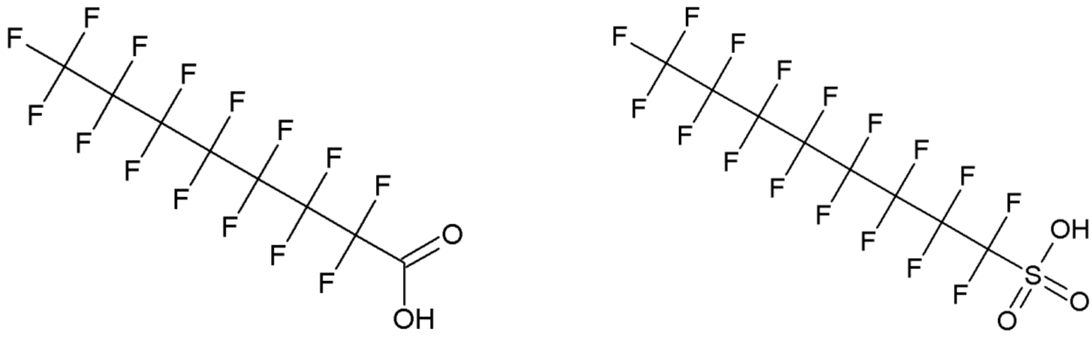
perfluorobutanoic acid

perfluorobutane sulfonate



perfluorohexanoic acid

perfluorohexanoic sulfonate



perfluorooctanoic acid

perfluorooctane sulfonate

Figure 2.16. Chemical structure of main PFCs

Precursor substances such as perfluorooctane sulfonamide-ethanols, perfluorooctane sulfonamides, and perfluorooctane sulfonamide acetic acids may contribute to the formation of PFOS during wastewater treatment processes (Higgins et al., 2005; Sinclair and Kannan, 2006). PFOA is a synthetic perfluorinated carboxylic acid and is less bioaccumulative than PFOS (Kannan et al., 2005). PFOA has been manufactured since the 1940s at industrial level and it can be formed from biodegradation of precursors such as fluorotelomer alcohols (Dinglasan et al., 2004). PFOA is used in the production of fluoropolymers (Olsen et al., 2005). Along with PFOS, PFOA has potential toxicity to cause liver cancer, affects the lipid metabolism and disturbs the immunity system of living organisms and provokes human infertility (Zhang et al., 2008; Fei et al., 2009).

PFBS is a homologous compound of PFOS that has been commercialized recently as an alternative to PFOS in a variety of applications. The shorter carbon chain makes PFBS less bioaccumulative compared to PFOS. Generally, short-chain PFCs (less than seven carbon atoms) are less toxic, show a higher mobility in the environment and have a lower bioaccumulation potential (Newsted et al., 2008). As they have been used for a relatively short time, there are very limited data on their fate in the environment.

2.4.2.2. Physicochemical properties

Physicochemical properties of six PFCs: perfluorobutanoic acid (PFBA), perfluorobutane sulfonate (PFBS), perfluorohexanoic acid (PFHxA), perfluorohexane sulfonate (PFHxS), perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), are summarised in Table 2.5. Water solubility of the selected PFCs ranges over two orders of magnitude. As can be seen, the highest solubility has PFCs with the shortest carbon chain, such as PFBS, whereas PFHxS and PFOS, with 6 and 8 C-F bonds, respectively, show the lowest solubility (1.4 and 0.57 g L^{-1}, respectively).

Table 2.5. Main physicochemical properties of the PFCs

PFC	CAS	Mw ($g\ mol^{-1}$)	Water solubility[a] ($mg\ L^{-1}$)	Log K_{ow}[a]
Perfluorobutanoic acid	375-22-4	214	nd	2.3
Perfluorobutane sulfonate	375-73-5	299	46.2	2.7
Perfluorohexanoic acid	307-24-4	314	15.7	3.1
Perfluorohexane sulfonate	108427-53-8	400	1.4	4.3
Perfluorooctanoic acid	335-67-1	414	3.4	4.6
Perfluorooctane sulfonate	2795-39-3	499	0.57	5.3

[a] - (Deng et al., 2012)

nd - not detected

Not only the C-atoms, but also hydrophilic part of the molecule influenced the solubility of these molecules. For example between PFOS and PFOA, with same number of C-atoms, water solubility of PFOS is much lower than for PFOA, indicating that PFOA is more polar compound due to presence of carboxylic group. In general, the PFCs with sulphonic group are more hydrophobic showing higher log K_{OW} values, than those with carboxylic groups when they contain the same number of carbon atoms in the molecules. For perfluorinated compounds with the same functional group, those with longer C-F chain are more hydrophobic.

The values of pK_a for PFCs are low, $pK_a < 1$ and hence, these compounds are in the anionic forms present in the neutral water solutions. The effects of environmental pH variation on the speciation of these compounds can be negligible.

Hence, large differences in the physicochemical properties of PFCs with varying carbon chain length and hydrophilic functional groups makes it difficult to predict their distribution in the environment (Rayne and Forest, 2010).

2.4.2.3. Determination techniques

Analytical methods to determine PFCs are based on liquid chromatography coupled to mass spectrometry (LC-MS) or tandem mass spectrometry (LC-MS/MS), with high sensitivity, peak resolution and increased efficiency and short analysis time (Onghena et al., 2012).

2.4.2.4. Environmental distribution

Perfluorinated compounds can be released into the environment directly from industrial wastes (fluorochemical production facilities or indirectly through the decomposition of other substances that may degrade to form PFCs) (Prevedouros et al., 2006). PFCs have been found in wastewater (Sinclair and Kannan, 2006; Zareitalabad et al., 2013), sewage sludge (Yoo et al., 2009; Yu et al., 2009; (Llorca et al., 2011; Sun et al., 2011; Yan et al., 2012), soils (Washington et al., 2007; Wang et al., 2013), sediments (Bao et al., 2009; Naile et al., 2010), surface water and groundwater (Enevoldsen and Juhler, 2010), aquatic organisms (Fernández-Sanjuan et al., 2010) and river waters (Hansen et al., 2002; Takino et al., 2003). In sediments from the USA, the Netherlands and several Scandinavian countries, PFOA was found in concentrations of hundreds pg g^{-1} range.

PFCs are considered as a new generation of contaminants that are globally distributed in the environment, and the routes of their entrance into sewage sludge remain unclear. Possible routes include the washing residues from treated textiles and cooking ware and, direct and indirect residues of industrial production (Washington et al., 2008).

Wastewater treatment plants have been identified as a relevant pathway of PFCs releases into the environment (Higgins et al., 2005). In sewage sludges from Spain, PFOS and PFOA have been detected in the highest concentrations, i.e., from 30 - 120 ng g^{-1} sludge dry matter, followed by PFBS that was quantified in the concentration of about 10 ng g^{-1} sludge dry matter (Llorca et al., 2011). Concentration of PFCs in soil samples from Japan, Mexico and USA, was detected in ng g^{-1} levels, with the highest values found for PFOS and PFOA, ranging from

1 - 30 ng g^{-1} (Strynar et al., 2012). This data should be completed with still not available results of distribution of PFCs in soils, i.e., their potential mobility from soil to water resources and uptake by plants grown on these soils, to predict their environmental impact.

2.4.3. Interaction of APCs and PFCs with sewage sludge and soil

It is generally accepted that APCs and PFCs have strong interaction with the organic matter of environmental matrices. It is known that dissolved organic matter is also a relevant parameter affecting the availability of organic contaminants (Zhou et al., 2000). Hydrophilic and hydrophobic DOC can act as "carriers" of associated contaminants through the formation of soluble complexes. Nevertheless, there is scarce information available about the mechanism of the interaction between the organic matter in the solid phase of sludges and APCs.

Some information on the sorption behaviour of NP in soils is provided in a few previous works (Düring et al., 2002; Höllrigl-Rosta et al., 2003; Ying and Kookana, 2005). The results shown that NP's sorption was influenced by the content of the organic carbon in soils and the concentration of dissolved organic carbon (Höllrigl-Rosta et al., 2003). The sorption mechanisms of other APCs, in particular APEOs, have not been studied.

The mechanism of the interaction of PFCs with sewage sludge has been scarcely reported to date (Ochoa-Herrera and Sierra-Alvarez, 2008; Zhou et al., 2010; Zhang et al., 2013). From the available data, it is accepted that many factors, including physicochemical characteristics of PFCs and sludge properties (stabilization process, organic matter content, pH), influence the incorporation of PFCs in the sewage sludge. Besides the limited information about the sorption pattern of PFCs in sludge, up to now there are no available data about the sorption reversibility of PFCs in sludges.

To date, the interactions of PFCs with soils have been reported only in the several sorption studies with soil samples with a low organic matter content

(Higgins and Luthy, 2006; Johnson et al., 2007; Kwadijk et al., 2010; Ahrens et al., 2011; Chen et al., 2012; Chen et al., 2013). These studies highlighted the role soil organic matter. In addition to the very limited information about the mechanisms of the sorption of PFCs in soils, to the best of our knowledge there is no any available data about the sorption reversibility of PFCs from such samples.

2.5. Working plan

In the context of this doctoral thesis, and in order to develop its first objective, the leaching of alkylphenolic compounds, specifically NP, OP and NP_1EO, from sewage sludge samples originated from WWTPs was examined. As these samples also contained a significant amount of heavy metals (Cu, Ni, Pb, Zn and Cr), their leaching pattern was also examined in parallel. The related working plan was designed as follows:

- Selection of several fresh and dried sewage sludge samples from different origin, subjected to different digestion treatments in the WWTP, and characterisation in terms of main physicochemical properties, such as pH, OM, OC, DOC, etc.

- Application of a standard compliance test to sludge samples in order to characterise NP, OP and NP_1EO and heavy metals leaching rates.

- Correlation of the leachability of the target alkylphenolic compounds and heavy metals to sludge characteristics (pH, OC, DOC) and comparison of the leaching pattern of fresh *vs.* dried sludge samples.

The second major objective of the work was to study the sorption behaviour of NP and NP_1EO in soil samples with contrasted characteristics. After the application of sorption and desorption tests, the relationship between the results obtained and physicochemical properties of target compounds and soils was examined. The working plan for this objective comprised the following steps:

- Selection of soil samples, originally not contaminated by NP and NP_1EO, exhibiting different physicochemical characteristics, such as pH, OC, DOC.

- Application of sorption test to obtain sorption isotherms which served for evaluation of the possible role of the APC concentrations on the sorption.

- Fitting (linear and the Freundlich models) of sorption isotherms to quantitatively describe the sorption process and to derive solid-liquid distribution coefficients.

- Application of desorption test to study sorption reversibility of NP and NP_1EO in soils.

- Examination of the relationship between the obtained sorption and desorption parameters and the main physicochemical properties of target compounds and soil samples (such as organic carbon content, DOC) to explain sorption mechanisms.

- Derivation of K_{OC} values and their comparison for both NP and NP_1EO in soils.

The third main objective was to investigate the sorption behaviour of three of the most common perfluorinated compounds (PFOS, PFOA and PFBS) in sewage sludge and soil samples. After the application of sorption and desorption tests, the physicochemical parameters of compounds and samples affecting mostly the sorption mechanism were evaluated. To fulfil this objective, the working plan was designed as follows:

- Selection of sewage sludge and soil samples (including soils with higher OC content), which originally did not contain PFOS, PFOA and PFBS, and characterisation of selected samples in terms of pH, OC, DOC, etc.

- Application of sorption and desorption tests to obtain isotherms and to evaluate sorption and sorption reversibility of PFCs in samples of sewage sludge and soil.

- Fitting of sorption isotherms by the most common fitting models (the Freundlich and linear) to get the quantitative parameters of the sorption pattern.

- Examination of the relationship between the obtained sorption and desorption parameters and the main physicochemical properties of target compounds, such as hydrophobicity in order to explain the mechanism of the sorption behaviour.

- Estimation of sorption reversibility of PFOS, PFOA and PFBS in selected sewage sludge and soil samples.

- Derivation of K_{OC} values for PFOS, PFOA and PFBS sorption in soils and their comparison.

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Chapter 3. Interaction of alkylphenolic compounds with sewage sludges and soils

3.1. Introduction

The amount of sewage sludge derived from municipal WWTPs has continuously increased over recent decades due to the implementation of the Council Directive 91/271/EEC on urban wastewater treatment (CEC, 1991). In the European Union, annual sewage sludge production rose from 5.5 million tonnes dry matter of sludge in 1992 to 9 million tonnes in 2006 (EWPCA, 1997; Magoarou, 2000). The highest amounts are produced by Germany, followed by the UK, France, Spain and Italy (Laturnus et al., 2007). Each of these five countries produces more than 500000 tonnes dry weight sludge per year, accounting for around 72% of the annual European sewage sludge production. In the last two decades in Europe, one of the main ways of sewage sludge disposal has become its application as organic fertilizer in agricultural soils. For the period 2003-2006, the proportion of sludge recycled in agriculture varied widely between different Member States and regions. In Denmark, Spain, France, Ireland, and the UK, 50% or more of the sludge generated was applied to agricultural land while in other Member states it was less than 5% (i.e. Finland) or no application (i.e. Greece, Netherlands) (Milieu Ltd., WRc and RPA, 2010; Kelessidis and Stasinakis, 2012). Although sludge addition ensures an improvement in soil fertility by increasing the organic matter and nutrients content, when sludge is applied to the land, pollutants might accumulate in the soil and, following repeated applications of sludge, they could reach toxic concentrations which might contribute to the pollution of soil and, as a consequence, of groundwater and plants.

The application of sewage sludge in agricultural soils is regulated by the Directive 86/278/EEC that sets maximum limit values for heavy metals in sludge or sludge-treated soil. However, in the context of the revision process of this Directive it has been found that further information is urgently needed about the presence of emerging pollutants in the sewage sludge which could contaminate terrestrial and aquatic environment when the sludge is used in agriculture. Some documents on sludge developed by the European Union proposed limit values for concentrations of some organic compounds. Among them, the suggested threshold values for the sum of nonylphenol (NP), nonylphenol monoethoxylate (NP_1EO) and nonylphenol diethoxylate (NP_2EO) in sludge for use on land were firstly 50 mg kg^{-1} (EC, 2000) and, in a more recent document, 450 mg kg^{-1} (referenced in Milieu Ltd., WRc and RPA, 2010). These compounds are lipophilic degradation products of more complex alkylphenolic compounds (APCs), formed during the sludge digestion process carried out in WWTPs, and resistant to further biodegradation (Ahel et al., 1994). Moreover, they are considered endocrine disrupting compounds because they can interfere the normal functioning of hormone systems (Colborn et al., 1993).

The leaching of pollutants from sludge must be assessed to evaluate the environmental risks associated with sludge application in agriculture. The leaching of heavy metals from sludge samples has been widely studied, especially when sludge samples are mixed with soils. Metal leaching is pH-dependent and it is also affected by the physicochemical characteristics of the metal, the chemical composition of both sludge and soil, the sludge stabilisation process in WWTPs and the climate conditions when the sludge is applied to the agricultural soil (Fuentes et al., 2004; García-Delgado et al., 2007). Specifically, the organic matter and the dissolved organic carbon originating from the sludge play a significant role in enhancing the solubility of heavy metals in soils amended with sludge (Wong et al., 2001; Antoniadis and Alloway, 2002; Ashworth and Alloway, 2008; Kaschl et al., 2002; Parat et al., 2007).

Unlike for heavy metals, APCs studies have mainly been aimed at measuring their total content in wastewater (Céspedes et al., 2005; Sánchez-Avila et al., 2009) and sewage sludge (Ahel et al., 1994; Fountoulakis et al., 2005; Fernández-Sanjuan et al., 2009; González et al., 2010). Besides indicating the environmental risk derived from the presence of the APCs, some of the reported works suggested that sludge drying did not modify the total content of OP, NP and NP_1EO because these compounds have relatively high boiling points (approximately 300 °C) (Fernández-Sanjuan et al., 2009).

However, limited information about APCs leachability from samples of environmental interest have been reported (Öman and Hynning, 1993), although preliminary studies suggested that APCs leaching in sludge samples and in sewage sludge-amended soils could be as low as 5% of their total concentration (La Guardia et al., 2001; Kouloumbos et al., 2008). Therefore, to the best of our knowledge, there is scarce information available about the influence of some sludge parameters (dissolved organic carbon, particulate organic carbon), as well as the effect of a drying treatment, on the leaching pattern of APCs.

To evaluate the risk associated with the pollution of soils by organic pollutants, not only the total concentration of pollutants in soils must be considered, but also their interaction with soil components. To our knowledge, there are no available studies on the sorption-desorption behaviour of NP_1EO, whereas a few previous works provided some information on the sorption behaviour of NP in soils (Düring et al., 2002; Höllrigl-Rosta et al., 2003; Ying and Kookana, 2005).

In this Chapter, the interaction of APCs with sewage sludge and soil samples was investigated. In the first part, the leaching of OP, NP and NP_1EO was evaluated in five samples of fresh and dried sewage sludge by applying a standard compliance test based on aqueous extraction. Moreover, the leaching of heavy metals (Cu, Ni, Pb, Zn and Cr) was studied. The effects of several sludge parameters, as well as the influence of sludge drying on the pollutant leaching pattern were evaluated.

In the second part, the sorption behaviour of NP and NP_1EO was described and compared in five soils with contrasted physicochemical properties. Sorption and desorption isotherms were obtained for the two analytes in a wide range of concentrations, and fitted to appropriate simple models (Freundlich and linear) to propose suitable sorption and desorption parameters for each APC-soil combination. Besides, correlations between sorption and desorption parameters and main soil characteristics were examined.

3.2. Materials and methods

3.2.1. Reagents and standards

Milli-Q double deionised water was obtained from a water purification system (USF PureLaB Plus, Spain) (18.2 MΩ cm^{-1}). Calcium chloride, $CaCl_2 \cdot 2H_2O$ and sodium azide, NaN_3 (extra pure) were purchased from Merck (Darmstadt, Germany). Methanol gradient grade for liquid chromatography, cyclohexane and ethyl acetate were supplied by Merck (Darmstadt, Germany). Standards of 4-tert-octylphenol (OP), nonylphenol technical mixture (NP) and 4-nonylphenol-mono-ethoxylate (NP_1EO) were purchased from Dr. Ehrenstorfer (Cromlab, Spain). Main physicochemical properties of APCs selected for this study are shown in Table 2.3 of section 2.4.1.

Stock standard solutions of NP and NP_1EO of 0.01 g mL^{-1} were prepared in methanol. Working solutions of NP and NP_1EO for sorption and desorption experiments were prepared by appropriate dilution of the stock standards in ethyl acetate. All prepared solutions were stored at -18 °C in 20 mL glass vials with polyethylene caps (Sigma-Aldrich, Germany).

Isotopically labelled standard solutions of 4-n-nonylphenol D8 (NP-D8) and 4-nonylphenol-mono-ethoxylate D2 (NP_1EO-D2) were purchased from Dr. Ehrenstorfer (Cromlab, Spain), at concentrations of 100 and 10 μg mL^{-1}, respectively.

Standard stock solutions of Cu, Ni, Pb, Zn (Alfa Aesar, A Johnson Matthey, USA) and Cr ($K_2Cr_2O_7$, National Institute of Standards and Technology (NIST), USA) were prepared in 1% nitric acid at the concentration of 1 g L^{-1} and used for heavy metal determinations.

3.2.2. Sample collection and characterisation

3.2.2.1. Sewage sludge samples

Five sewage sludge samples (SL1 - SL5) were collected in WWTPs located in industrial zones in Catalonia, Spain. The SL1, SL2 and SL3 samples originated from highly industrial areas and were treated biologically through anaerobic digestion. The SL4 and SL5 samples were from less industrial zones and were not submitted to any digestion treatment. Samples were collected from the sludge tanks using pre-cleaned amber glass pots.

Each sludge sample was manually homogenised and divided into two portions. One portion was kept in the freezer (at −18 °C) without any further treatment; these portions were designated as the fresh sludge samples. The other portion was dried at 40 °C until constant weight and kept at room temperature in amber glass containers; these portions were designated as dried sludge samples.

Table 3.1 summarises the main sludge characteristics as well as the concentration of heavy metals, from aqua regia extracts, and the total content of APCs in the dried sludge samples, obtained in a previous work of the research group (Fernández-Sanjuan et al., 2009). This information was necessary for some calculations and interpretation of results. Dry matter of sludge samples was determined by drying 10 g of fresh sludge at 105 °C. The pH of sludge samples was measured in Milli-Q water, using a solution-to-sludge ratio of 2.5 mL g^{-1}. The content of organic matter (OM) was determined gravimetrically after combustion of 3 g of sludge at 550 °C. For the elementary analysis (total C and N), 2 mg of the dried sludge sample were weighed in tin containers with V_2O_5 as catalyst and introduced into an elemental organic analyser (Thermo Finnigan NA 2100, Italy). Organic carbon was determined by the same procedure after acid digestion with 4 mol L^{-1} HCl. DOC content was measured in the solution of sludge samples with 0.01 mol L^{-1} $CaCl_2$ (10 mL g^{-1}), using a Total Organic Carbon Analyzer

(TOC-5000A, Japan) with a previous acidification with HCl to pH 3 to remove the carbonates.

Heavy metals were analysed following ISO Norm 11466 for the determination of aqua regia soluble amounts (ISO, 1995a). The concentration of a few metals (such as Hg and Cd) were under the quantification limits, and the concentration of other heavy metals (Cu, Ni, Pb, Zn, and Cr) was below the threshold limits regulated in the Council Directive (CEC, 1986) and in the working document on sludge (CEC, 2000).

The total content of the three APCs investigated was obtained by ultrasonic extraction, including two steps with hexane/dichloromethane (1:1, v/v) and one step with dichloromethane/acetone (1:1, v/v), in a ratio of 100 mL per gram of dried sludge in each step. Extracts were subsequently cleaned up by solid phase extraction and analysed by Trace gas chromatography coupled to Trace mass spectrometry (Thermo Finnigan). Among the APCs investigated, OP had the lowest concentrations in the sludge samples examined (0.3–14.9 mg kg^{-1}), whereas the concentrations of NP and NP_1EO ranged from 3.8 to 187 and from 3.2 to 56 mg kg^{-1}, respectively (Table 3.1). The concentrations of NP in the SL1, SL2 and SL3 samples were higher than in the other two samples, most likely because of the anaerobic digestion process applied to corresponding WWTPs. Under these conditions, APCs are transformed to strongly lipophilic degradation products, particularly NP, that is resistant to further biodegradation (Ahel et al., 1994).

Table 3.1. Main physicochemical characteristics and the total content of heavy metals and alkylphenolic compounds (Value (SD); n = 3) in sewage sludge samples

Parameter	**SL1**	**SL2**	**SL3**	**SL4**	**SL5**
Physicochemical characteristics					
Dry matter (%)	21 (0.2)	28.7 (0.1)	17.2 (0.1)	13.9 (0.1)	16.1 (0.1)
pH	8.3 (0.1)	8.6 (0.1)	8.4 (0.1)	7.1 (0.1)	6.1 (0.1)
OM (%)	61.6 (0.1)	50.4 (0.6)	62.5 (0.8)	73.2 (0.1)	77.4 (0.2)
C[a] (%)	34	38	35	28	42
N[a] (%)	5.3	7.6	7.1	3.9	6.9
OC (%)	27.9 (0.2)	32.2 (0.1)	28.2 (0.3)	22.8 (0.1)	37 (1)
DOC (mg kg^{-1})	35900 (60)	21300 (100)	21400 (400)	53000 (1100)	70000 (2400)
Content of heavy metals extractable in aqua regia (mg kg^{-1} dry matter)					
Cu	425 (8)	666 (27)	635 (34)	631 (21)	528 (36)
Ni	73 (3)	25 (1)	94 (4)	29 (1)	16 (1)
Pb	86 (2)	59 (2)	41 (3)	73 (2)	65 (2)
Zn	140 (4)	455 (4)	1446 (84)	214 (19)	1210 (48)
Cr	135 (2)	137 (1)	150 (2)	119 (2)	52 (5)
Total content of alkylphenolic compounds (mg kg^{-1} dry matter)					
OP	14.9 (0.1)	1.6 (0.2)	1.9 (0.2)	0.29 (0.02)	0.64 (0.04)
NP	23 (1)	63 (3)	187 (4)	3.8 (0.2)	11 (1)
NP_1EO	12.1 (0.1)	19 (1)	56 (5)	3.2 (0.3)	13 (1)

[a] n = 1

3.2.2.2. Soil samples

Five soil samples (ASCO, ALM, GOLOSO, DELTA2 and OVI01) were collected from different areas in Spain. Samples were taken from the surface layer (0 - 10 cm depth), air-dried and sieved through a 2 mm mesh. Prior to analysis, samples were homogenized with a roller table and stored at room temperature. The main physicochemical properties of the soils examined in this study are summarized in the Table 3.2.

The particle size distribution was determined by the pipette method (Burt, 2004). The pH of soil was measured in Milli-Q water, using a solution-to-soil ratio of 2.5 mL g^{-1}. The cation exchange capacity (CEC) was determined from the sum of the extractable bases plus the extractable acidity obtained by displacement with $BaCl_2$-triethanolamine (TEA) solution buffered at pH 8.2 (Burt, 2004). Contents of total carbon and organic carbon (OC) were determined by elemental organic analyzer Thermo EA 1108 (Thermo Scientific, Milan, Italy) with a He flow rate at 120 mL min^{-1} (ISO, 1995b). The organic carbon content was analysed with the samples previously treated by HCl to eliminate the carbonates and using tin capsules and V_2O_5 as additive. The carbonate content was determined by using the calcimeter Bernard method (Mueller and Gastner, 1971). DOC content was measured in soil solution with 0.01 mol L^{-1} $CaCl_2$ in the ratio L/S of 10:1, using a Total Organic Carbon Analyzer (TOC-5000A, Shimadzu, Japan), with a previous acidification to pH 3 with HCl to remove carbonates.

Table 3.2. Main soil characteristics

Soil sample	Clay content	Sand content	pH	CEC	C	$CaCO_3$	OC	DOC	$\frac{DOC}{OC}$
	(% with respect to mineral matter)			($cmol_c$ kg^{-1})	(%)	(%)	(%)	(mg kg^{-1})	
ASCO	17.2	18.9	8.0	42.8	6.0	38	0.2	184	0.092
ALM	10.9	56.4	5.9	23.4	1.9	2	1.6	451	0.028
GOLOSO	10.4	78.0	6.3	72.4	3.6	4	3.9	574	0.015
DELTA2	43.6	15.8	7.9	89.3	13.9	51	7.7	777	0.010
OVI01	23.6	51.7	4.6	46.3	9.5	3	9.4	5741	0.061

Particle size analysis showed that the clay content was higher than 10% in all soil samples. According to the USDA criteria, ASCO soil had a silt loamy texture, ALM and GOLOSO soils, with different OC contents, were sandy loam soils, whereas DELTA2 and OVI01 soils, with the highest OC within the soils studied here, were clay loamy and loam soils, respectively.

Several soils were acidic (ALM, GOLOSO and OVI01) with $CaCO_3$ lower than 4%, whereas ASCO and DELTA2 soils were basic with a high content of $CaCO_3$. Whereas the content of elemental carbon varied within one order of magnitude (from 1.9 in ALM to 13.9% in DELTA2), organic carbon varied within a nearly two orders of magnitude range (from 0.2 in ASCO soil up to 9.4% in OVI01).

The DOC content ranged from 184 in ASCO up to 5741 mg kg^{-1} in OVI01. Ratios of DOC *vs.* OC were calculated and are also shown in Table 3.1. The highest DOC/OC ratio was found in the ASCO soil, which had the lowest OC content but the highest pH. Despite the low pH of the OVI01 soil, the OC content was relatively soluble and its DOC/OC ratio was the second among the soils investigated.

3.2.3. Leaching test applied to sewage sludge samples

A standard compliance test was used to obtain the sewage sludge sample leachates in the established liquid–solid ratio of 10 mL g^{-1} (CEN, 2002). For the dried sludge samples, 8 g of sludge sample was mixed with 80 mL of double deionised water in a glass tube. For the fresh sludge samples (with water content from 71 to 86 %), a higher weight sample was taken to obtain 8 g of dry matter. The sample mass was corrected for its respective water content, and the quantity of water added varied accordingly to reach a liquid–solid ratio of 10 mL g^{-1}. The suspensions were shaken end-over-end (60 rpm) for 24 h in glass tubes and centrifuged for 30 min at 450 *g*. The resulting supernatants, i.e. sludge leachates, were stored for further analyses.

The leaching yields of heavy metals and APCs were calculated using the concentration found in the aqua regia extracts and the total content, respectively, both determined in the dried sludge samples (Table 3.1).

As mentioned earlier, the leaching of heavy metals was investigated although the total concentration of heavy metals was below the threshold limits regulated. Regarding APCs, as the sum of the NP and NP_1EO concentrations exceeded the proposed threshold limit of 50 mg kg^{-1} (CEC, 2000) in many sludge samples (see Table 3.1), the study of their leaching was fully justified. On the contrary, the leaching of NP_2EO was not evaluated since this compound was not detected in the sewage sludge samples analysed here.

3.2.3.1. Characterisation of sludge leachates

A 20-mL aliquot of the sludge leachate was liquid–liquid extracted with cyclohexane (20 mL) under conditions similar to those used to determine the APC concentrations (Navarro et al., 2009). The organic extract was analysed by gas chromatography–mass spectrometry (GC-MS) operating in a full-scan mode under the conditions described below. Different classes of organic compounds (aromatic alcohols, aliphatic carboxylic acids, polycyclic aromatic compounds, sulphur compounds and sterols) were identified using the National Institute of Standards and Technology (NIST 08) data library. The match between the experimentally obtained and theoretical mass spectra was higher than 90%. The quantification of APCs in these leachates is described below.

Another 20-mL aliquot of the sludge leachate was lyophilised with a laboratory freeze drier (Telstar Lioalfa 6, Spain) operating at a working temperature of −40 °C and a pressure of 5×10^{-2} mbar. The resulting lyophilised sludge leachate was analysed with a Fourier Transform Infrared (FT-IR) spectrometer (Thermo Scientific Nicolet iS10, USA). The wavelength range was between 650 and 4,000 cm^{-1} and the spectral resolution was 4 cm^{-1}. Additionally, the lyophilised sludge leachates were analysed for total organic carbon (OC) with an elemental organic analyser (Thermo EA 1108, Thermo Scientific, Italy) set to a He flow rate of 120 mL min^{-1}, a combustion furnace temperature of 1000 °C and a chromatographic column oven temperature of 60 °C, with an oxygen loop of 10 mL at 100 kPa using tin capsules and V_2O_5 as additive (ISO 1995).

The DOC content was quantified in 0.45 µm polyamide filtered sludge leachates with a Total Organic Carbon Analyser (TOC-5000A, Japan). Samples had been previously acidified to pH 3 with HCl to remove carbonates. Quantifying the DOC allowed us to estimate the particulate organic carbon (POC) content in the sludge leachates, thus defining the POC as the difference between the TOC and DOC values.

3.2.4. Sorption and desorption tests applied to soils

Three grams of dry soil were suspended in a glass tube with 0.01 mol L^{-1} $CaCl_2$, in liquid to solid ratio of 10 mL g^{-1}, according to the OECD guideline (2000). Additionally, 0.03 g of NaN_3 was added as a biodegradation inhibitor. The resulting suspension was end-over-end shaken for 24 hours and after this pre-equilibration time, nine different volumes of the NP or NP_1EO working solutions were added to cover a range of initial concentrations from 0.03 to 270 µg mL^{-1} for NP and from 0.2 to 70 µg mL^{-1} for NP_1EO. The suspensions were further shaken for 24 hours at 60 rpm, and then centrifuged for 30 min at 450 *g*. The supernatants were decanted off and filtered through 0.45 µm polyamide filters. For the subsequent desorption experiments, some of the soil residues resulting from sorption experiments (at least four initial concentrations of the range of NP or NP_1EO concentrations assayed), were dried at 40 °C during 48 h. Then, 30 mL of 0.01 mol L^{-1} $CaCl_2$ were added to the dried soil residue and after shaking for 24 h the resulting suspension was centrifuged and treated as in the sorption test.

3.2.5. Determination of heavy metals in sludge leachates

The heavy metal concentration of filtered sludge leachates was quantified using an inductively coupled plasma optical emission spectrometry (ICP-OES) instrument (Perkin-Elmer, Optima 3200RL, USA) equipped with an auto sampler (Perkin-Elmer AS-90 Plus, USA). This equipment contained a radiofrequency source (working at 1,150 W and a frequency of 40 MHz), a cross-flow nebuliser and a segmented-array charge coupled device detector. The emission lines (in nanometres) were used as follows: Cu—324.752, Ni— 231.604, Pb—220.353, Zn—213.857 and Cr—267.716. The detection limits of the ICP-OES measurements were 0.01 mg L^{-1} for Cu and Cr, 0.1 mg L^{-1} for Ni, 0.2 mg L^{-1} for Pb and 0.025 mg L^{-1} for Zn.

3.2.6. Determination of alkylphenolic compounds

To quantify the OP, NP and NP_1EO in samples, 0.5 µg of each internal standard (NP-D8 or NP_1EO-D2) were added to 30 mL of the sludge or soil solutions obtained from respective leaching or sorption and desorption tests. The solutions were subsequently liquid–liquid extracted with 30 mL of cyclohexane with manual shaking of solutions for two min. The organic extracts were transferred to an amber glass vial and evaporated in a N_2 stream (Pierce, Reacti-Vap, TM III, USA) at 50 °C to a final aliquot of approximately 0.5 mL. This aliquot was transferred into a 2 mL chromatographic amber vial (Agilent, Germany), evaporated to dryness by N_2 and reconstituted with ethyl acetate to a final volume of 1 mL.

The efficiency of the liquid–liquid extraction with cyclohexane was determined by extracting known amounts of OP, NP, NP_1EO, NP-D8 and NP_1EO-D2 in 30 mL of double deionised water. Arithmetic means of triplicate measurements showed that the recoveries for APCs and internal standards ranged from 90 to 110% with relative standard deviations lower than 10%, thus indicating the optimal extraction efficiency.

The OP, NP and NP_1EO concentrations in standard solutions and samples derived from leaching and sorption-desorption experiments, were determined using gas chromatography (GC) (Agilent, 6890 Series, USA) coupled to a quadrupole mass spectrometer (MS) (Agilent Mass Selective Detector 5973, USA) with the electron ionisation set at 70 eV. A fused-silica capillary column (HP 5MS) was used at a flow rate of 1.1 mL min^{-1} with helium as the carrier gas. An extract volume of 2 µL was injected in splitless mode. The injector temperature was set at 200 °C. The oven was set to an initial temperature of 70 °C and maintained there for 1 min. The oven temperature was then raised to 206 °C at a rate of 8 °C min^{-1}. Then, the temperature was raised at a rate of 6 °C min^{-1} to 310 °C. The temperature was maintained at 310 °C for 10 min. The total run time was approximately 45 min.

Acquisition was performed using time-scheduled selected ion monitoring (SIM) with three retention time windows. APCs were identified by their fragmentation ions in mass spectra. The monitored ions (m/z) used for the quantification and confirmation of each target compound and internal standards are presented in Table 3.3. NP, NP_1EO and NP_1EO-D2 appeared in the chromatogram as a mixture of isomers (peak cluster).

Table 3.3. Characteristic ions for GC-MS analysis of OP, NP, NP_1EO, NP-D8 and NP_1EO-D2

APC	**Retention time (min)**	**Quantification ion (m/z)**	**Confirmation ion (m/z)**
OP	11.0	135	107, 207
NP	12.4 - 13.2	135	107, 149
NP_1EO	15.4 - 16.4	179	135, 193
NP-D8	14.6	113	112, 228
NP_1EO-D2	15.4 - 16.7	181	195

The most abundant fragmentation ions resulted from the cleavage of bonds mainly in alkyl chain. Thus, as an example the most intensive peak at m/z 135 is caused by the favoured rupture of the octyl- or nonyl- chain from OP and NP, respectively, and further elimination of this ion for two methylene groups produces an abundant ion at m/z 107. Another abundant ion for NP with m/z of 149 corresponds to the loss of pentyl group from the molecular ion. In the mass spectra of NP_1EO the base peak at m/z equal to 179 is attributed to the addition of one ethoxylate group to the most intensive peak of NP corresponding to the m/z 135.

Figures 3.1 and 3.2 show the SIM chromatograms obtained for a standard APC-solution. The SIM chromatogram of the analysed APCs in a sewage sludge sample is shown in Figure 3.3.

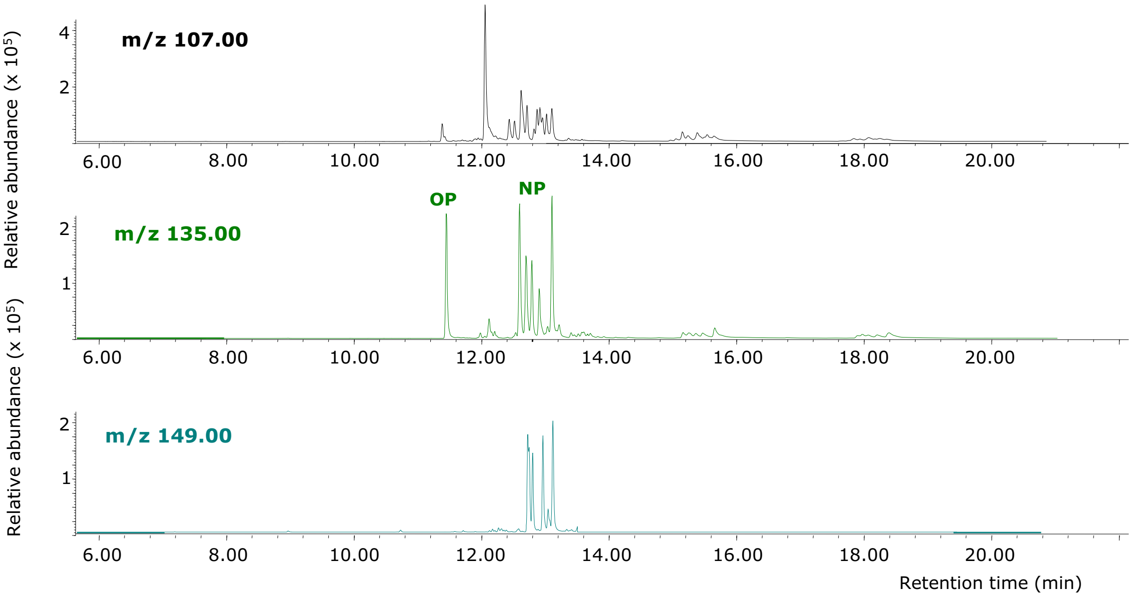

Figure 3.1. SIM chromatograms obtained for a standard solution of OP (2.3 µg mL^{-1}) and NP (25.6 µg mL^{-1})

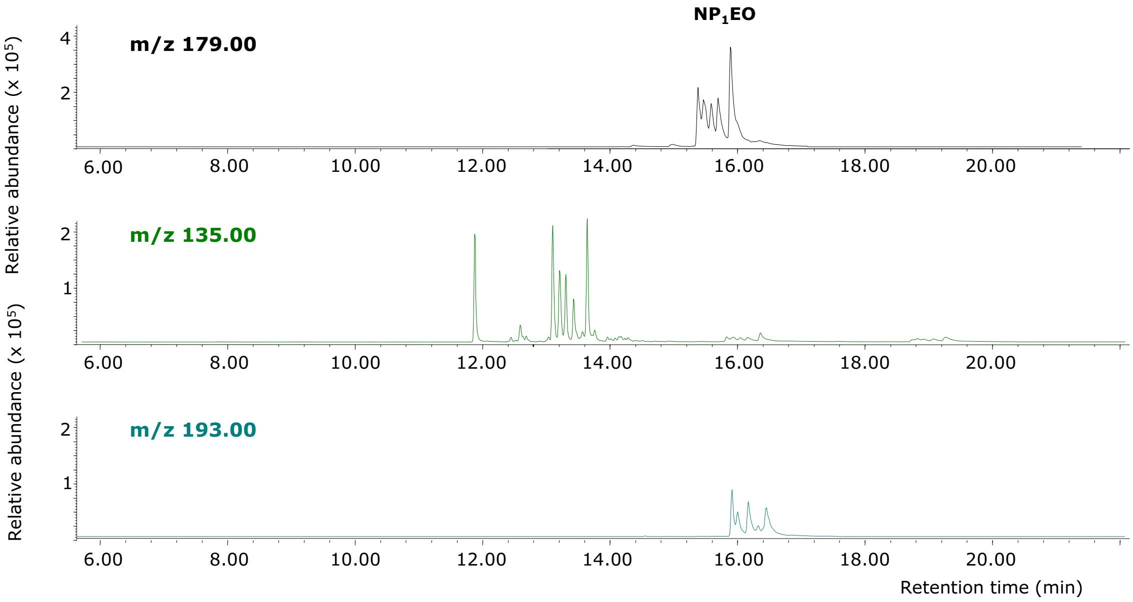

Figure 3.2. SIM chromatograms obtained for a standard solution of NP$_1$EO (12.4 µg mL^{-1})

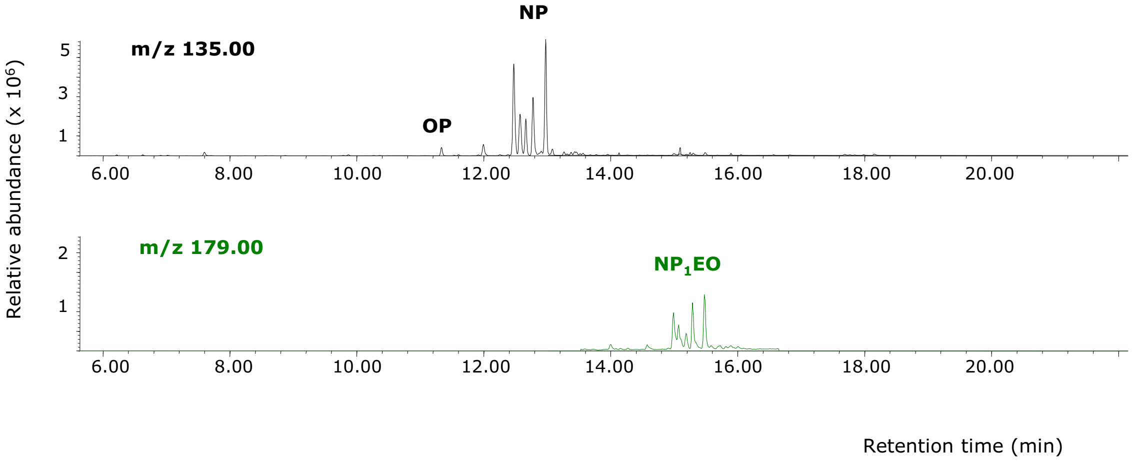

Figure 3.3. SIM chromatogram obtained for the dried SL3 sludge sample

3.2.6.1. Quality parameters of calibration

Seven-point calibration curves were built up over a concentration range from 0.02 to 2.3 μg mL^{-1} for OP, from 0.03 to 26 μg mL^{-1} for NP and from 0.03 to 12.4 μg mL^{-1} for NP_1EO. NP-D8 was used as an internal standard to quantify OP and NP, and NP_1EO-D2 to quantify NP_1EO. The quality parameters of the method, such as slope of the calibration curve and its reproducibility, limits of detection, as well as long term reproducibility are shown in Table 3.4.

The calibration curves had satisfactory correlation coefficients ($R^2 > 0.99$) for the three APCs. As can be seen in Table 3.4, the higher slopes of the calibration curves for OP and NP indicated a higher sensitivity of GC-MS for the determination of these compounds, in comparison with ethoxylated APC. The relative standard deviation (RSD) of the slopes was lower than 8% for the three compounds.

Table 3.4. Quality parameters of the calibration of the APCs analysis

Quality parameter	**Sample**	**OP**	**NP**	**NP_1EO**
Slope (% RSD, n=3)		4.4 (6)	3.0 (2)	1.7 (8)
LOD_{instr} (μg mL^{-1} in measurement vial)		0.00007	0.007	0.008
LOD_{method} (μg mL^{-1} in leachate/contact solution)	sludge	0.00003	0.001	0.005
	soil	nd	0.001	0.004
$Reproducibility_{instr.}$ (% RSD, n=5)		3	4	4
$Reproducibility_{method}$ (% RSD, n=3)	sludge	2-10	3-15	5-15

na - not determined

The limit of detection (LOD) was calculated as the concentration of APC that yielded a signal-to-noise ratio of three (the ratio between the peak intensity and the noise). The instrumental detection limit ($LOD_{instr.}$) was calculated from the chromatogram of the standard solution with the lowest concentration for each compound, and in Table 3.4, is referred to the concentration of APC in the vial of measurement. The limit of detection of the leaching method (LOD_{method}) used for sludges was calculated from the SIM chromatogram of the leachate of the SL4 dried sludge sample and, in Table 3.4, it is referred to the minimum concentration of APC that can be detected in the sludge leachate. The LOD_{method} for the sorption experiment was calculated from the contact solution of the sorption experiment of ASCO soil sample and, in Table 3.4, it is referred to the minimum concentration of APC that can be detected in the soil contact solution. LOD_{method} were very similar between two matrices.

Long-term reproducibility of the measurement ($Reproducibility_{instr.}$) was calculated as the relative standard deviation of five determinations in different days, of a standard solution of 0.05 µg mL^{-1} of each APC. The long-term reproducibility of the method ($Reproducibility_{method}$) was calculated as the relative standard deviation of three analyses performed for each APC in the sludge samples and is given as a range for each compound (Table 3.4). Reproducibility was reasonable with RSD values between 2 and 15%.

3.2.6.2. Quality control of the analysis

Blank samples were run in parallel to ensure that samples did not contain the target compounds. Furthermore, a control test was run in 0.01 mol L^{-1} $CaCl_2$ solution containing 6.2 µg mL^{-1} NP, 6.5 µg mL^{-1} NP_1EO, 0.5 µg mL^{-1} NP-D8 and 0.5 µg mL^{-1} NP_1EO-D2 and GC-MS results showed that there were no losses of target analytes due to the sorption on the material used or degradation.

3.2.7. Quantification of sorption and desorption parameters

The sorption solid-liquid distribution coefficient, K_d (mL g^{-1}) was calculated as the ratio between the concentration of the target APC (NP or NP_1EO) sorbed in the soil, C_s (µg g^{-1}) and the concentration of the APC in the aqueous phase at the equilibrium, C_{eq} (µg mL^{-1}):

$$K_d = \frac{C_s}{C_{eq}} \tag{3.1}$$

C_{eq} values were directly determined by GC-MS, whereas C_s was calculated by the following equation:

$$C_s = \frac{(C_{in} - C_{eq})\cdot V}{m_s} \tag{3.2}$$

where C_{in} (µg mL^{-1}) corresponds to the initial concentration of the APC in the solution added to the soil sample, V (mL) is the volume of aqueous phase and m_s (g) refers to the dry mass of soil sample.

Similar to K_d (Eq. 3.1), the desorption solid-liquid distribution coefficient, $K_{d,des}$ (mL g^{-1}) was calculated as follows:

$$K_{d,des} = \frac{C_{s,des}}{C_{eq,des}} \tag{3.3}$$

where $C_{s,des}$ (µg g^{-1}) and $C_{eq,des}$ (µg mL^{-1}) are, respectively, the APC concentration in the solid phase and in the liquid phase after the desorption experiment. $C_{eq,des}$ values were directly determined by GC-MS, whereas $C_{s,des}$ were calculated as the difference between the initial concentration of the APC in the soil residue resulting from the sorption experiment, $C_{in,des}$ (µg g^{-1}), and the APC desorbed referred to the mass of soil as follows:

$$C_{s,des} = C_{in,des} - \frac{C_{eq,des} \cdot V}{m_s} \qquad (3.4)$$

$C_{in,des}$ is the concentration of APC sorbed in the soil after the sorption experiment (C_s), corrected, when required, by the amount of APC present in the residual volume of solution ($C_{eq} \cdot V_{res}$) that remained in the soil after the sorption experiment:

$$C_{in,des} = C_s + \frac{C_{eq} \cdot V_{res}}{m_s} \qquad (3.5)$$

Finally, the desorption yield, D (%), was calculated from the ratio between the amount of APC desorbed and the amount of APC present in the soil previously to desorption experiment, as follows:

$$D\ (\%) = \frac{C_{eq,des} \cdot V}{C_{in,des} \cdot m_s} \cdot 100 \qquad (3.6)$$

3.2.8. Fitting of sorption and desorption isotherms

Sorption and desorption isotherms were constructed by plotting C_s *vs.* C_{eq} and $C_{s,des}$ *vs.* $C_{eq,des}$ of the target compound. Isotherms were fitted to the Freundlich and linear models.

The Freundlich sorption and desorption isotherms are quantitatively described by the respective following equations:

$$C_s = K_F \cdot (C_{eq})^N \qquad (3.7)$$

$$C_{s,des} = K_{F,des} \cdot (C_{eq,des})^{N_{des}} \qquad (3.8)$$

where K_F and $K_{F,des}$, whose units depend on N values, are the Freundlich constants of the respective process, which express the affinity of a compound to a given solid sorbent, here the soil sample, and N is an empirical parameter that describes the degree of isotherm non-linearity. When N is approximately equal to 1, the Freundlich model can be assumed as linear, and in that case the value of K_F approaches to a value of K_d and $K_{F,des}$ to a value of $K_{d,des}$ valid for all the concentration range tested (Eqs. 3.1 and 3.3, respectively).

Sorption and desorption isotherms could also be fitted to a linear equation in most cases, described by a constant slope between C_s *vs.* C_{eq} and $C_{s,des}$ *vs.* $C_{eq,des}$ in all the concentration range investigated. In these cases, K_d and $K_{d,des}$ were deduced directly from the slope of isotherms.

The K_F and N parameters of the Freundlich model were calculated for the sorption isotherms, using the Solver function of Microsoft Excel™, by minimizing the residual root mean square error (RMSE), which for *m* experimental data points and *p* adjustable fitting parameters is defined by (Kinniburgh, 1986):

$$\mathrm{RMSE} = \left(\frac{\mathrm{RSS}}{m - p}\right)^{½} \qquad (3.9)$$

where RSS is the residual sum of squares, which for *m* experimental data is given by the following equation:

$$\mathrm{RSS} = \sum_{i=1}^{m} \frac{\left(C_{s,exp,i} - C_{s,cal,i}\right)^2}{\left(C_{s,cal,i}\right)^2} \qquad (3.10)$$

where $C_{s,exp,i}$ and $C_{s,cal,i}$ are the experimental and calculated sorbed concentration, respectively. The parameters of the Freundlich model for the desorption isotherms were calculated in the same way from the $C_{s,des,exp,i}$ and $C_{s,des,cal,i}$ data.

The standard error of the fitting parameters was estimated by using the SOLVSTAT.XLS of Microsoft Excel^{TM}.

3.3. Results and discussion

3.3.1. Leaching of heavy metals and alkylphenolic compounds from fresh and dried sewage sludge

3.3.1.1. Characterisation of sludge samples: implications for the pollutant leaching pattern

The main characteristics of the sludge samples and sludge leachates are summarised in Table 3.5. The dry matter in the fresh sludge samples ranged from 14 to 29%. The total carbon and the total organic carbon ranged from 28 to 4% and from 23 to 37%, respectively. Fresh sludge leachates were slightly basic, with pH values ranging from 7.6 to 7.8. In contrast, the leachates of dried sludge samples were either neutral or slightly acidic with pH values from 6.0 to 7.1. Moreover, leachates from the dried sludge samples showed higher DOC values (21300 to 70000 mg kg^{-1}) than from fresh samples (12200 to 35800 mg kg^{-1}). This finding agrees with previously reported data in which higher concentrations of soluble organic compounds was found in soils amended with dried sewage sludge than in soils amended with non-dried, composted sewage sludge (Fernández et al., 2007), which was attributed to the increase in the microbial degradation due to the thermal treatment, leading to higher concentrations of dissolved organic compounds (such as amino acids and carbohydrates).

The DOC and pH values in the leachates of dried sludge samples were inversely correlated ($R^2 = 0.94$, $P = 0.01$), confirming that the increase in the concentration of soluble organic compounds resulting from the drying of the sludge caused a decrease in the pH leachates of the dried sludge samples. In contrast, variations in the DOC of leachates from fresh sludge samples could not be explained by changes in pH, most likely because their pH values were basic and varied within a narrow range. The decrease in pH and increase in DOC after drying the samples may cause an increase in metal leaching. This hypothesis is tested as described below.

Drying treatment also yielded differences in the TOC values of the sludge leachates. The TOC values decreased around 40% (SL1), increased around 50% (SL4) or remained reasonably constant (SL2, SL3 and SL5) after the drying treatment. For all sludge samples, the TOC values were much higher than the DOC values in leachates originating from fresh sludge samples (TOC=2.1 (0.4) x DOC; R^2 =0.89, P =0.02), whereas the TOC and DOC values were much more similar in leachates obtained from dried sludge samples (TOC=1.0 (0.1) x DOC; R^2 =0.95, P =0.01). These correlations indicate that the relative amount of POC was higher in fresh sludge samples (>50% of TOC) than in dried sludge samples (a maximum of 25% of TOC, with SL1 and SL4 having negligible POC values). Both variables correlated well in fresh sludge samples (TOC=1.6 (0.2) x POC; R^2 =0.94, P =0.01). The drying treatment decomposed the organic compounds in the leachates into molecules that are simpler, smaller, and less hydrophobic, which is consistent with previously reported data (Gigliotti et al., 2002; Cox et al., 2004). Therefore, because the drying treatment modified the nature of the solubilised organic compounds, it can be expected that the leaching pattern of the APCs would also change. This hypothesis is discussed in a later section.

.5. Sludge and sludge leachates characteristics

cteristic	**Sludge treatment**	**SL1**	**SL2**	**SL3**	**SL4**	**SL5**
tter (%)	Fresh	21.0 (0.1)	28.7 (0.1)	17.2 (0.1)	13.9 (0.1)	16.1 (0.1)
arbon (%)^{a}	Dried	34	38	35	28	42
)	Dried	27.9 (0.2)	32.2 (0.1)	28.2 (0.3)	22.8 (0.1)	37 (1)
leachate						
	Fresh	7.8 (0.3)	7.7 (0.1)	7.6 (0.1)	7.7 (0.3)	7.6 (0.2)
	Dried	6.7 (0.1)	7.1 (0.1)	6.8 (0.1)	6.2 (0.1)	6.0 (0.1)
g kg^{-1})	Fresh	16500 (1900)	12200 (500)	12300 (400)	16100 (2400)	35800 (900)
	Dried	35900 (60)	21300 (100)	21400 (400)	53000 (1100)	70000 (2400)
mg kg^{-1})	Fresh	53040	25300	32400	36000	80400
	Dried	32200	27400	28400	53500	78400

The main assumptions drawn by the changes in DOC, TOC and POC were confirmed by the FT-IR analyses, which also helped to examine the effect of the drying treatment on the organic compounds of the sludge leachates. The spectra plotted in Figure 3.4 (which, as an example compare the FT-IR spectra of leachates originating from fresh and dried SL1 sludge samples) illustrate the differences between the hydrophobic and hydrophilic functional groups in fresh and dried sludge samples.

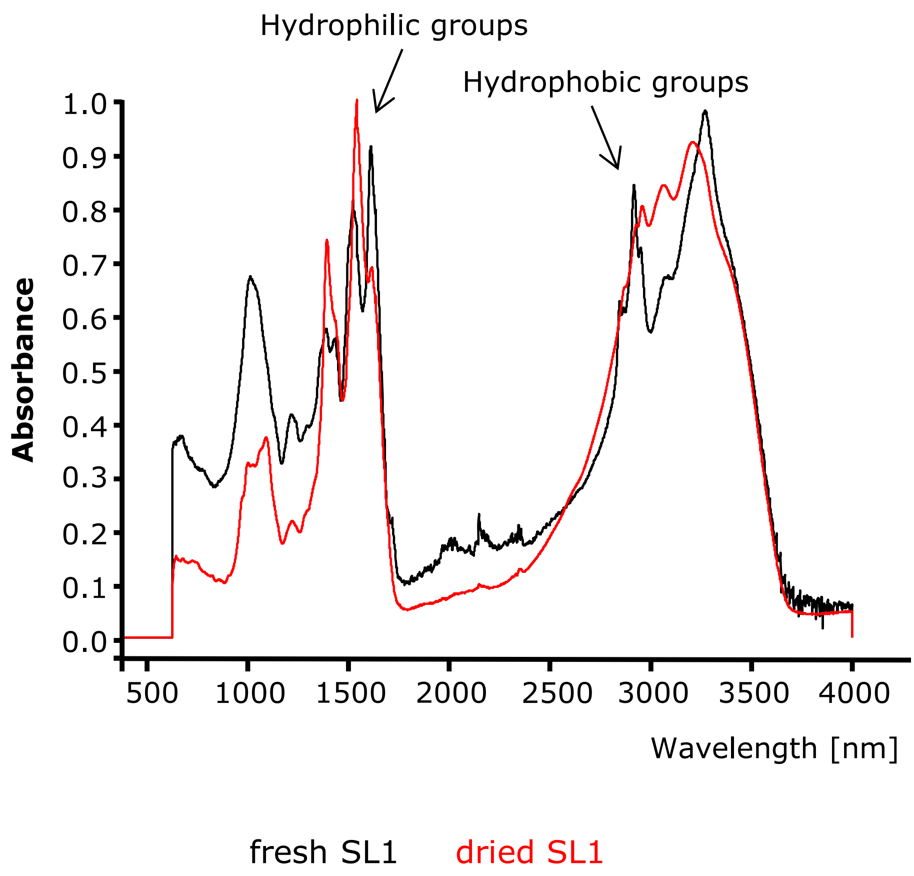

Figure 3.4. FT-IR spectra of leachates obtained from fresh and dried SL1 sludge samples

The narrow band at 2800–3000 cm^{-1} corresponding to hydrophobic CH-groups, was much higher in leachates from fresh sludge samples, confirming their more hydrophobic character. In contrast, the bands at approximately 1400–1550

cm^{-1}, which correspond to hydrophilic CO-functional groups, were more intense for the dried sludge leachates.

The TOC of the sludge leachates was further investigated with full-scan GC-MS. The qualitative and quantitative analyses, as shown in Figure 3.5 and Table 3.6, confirmed that the relative abundance of the organic compounds, some of them with log K_{OW} values similar to those values of the APCs established by Ahel and Giger (1993a) (between 4.1 and 4.5), was generally higher in leachates originating from fresh sludge samples. This fact suggested that APCs might also be present in larger amounts in the leachates of fresh sludge samples.

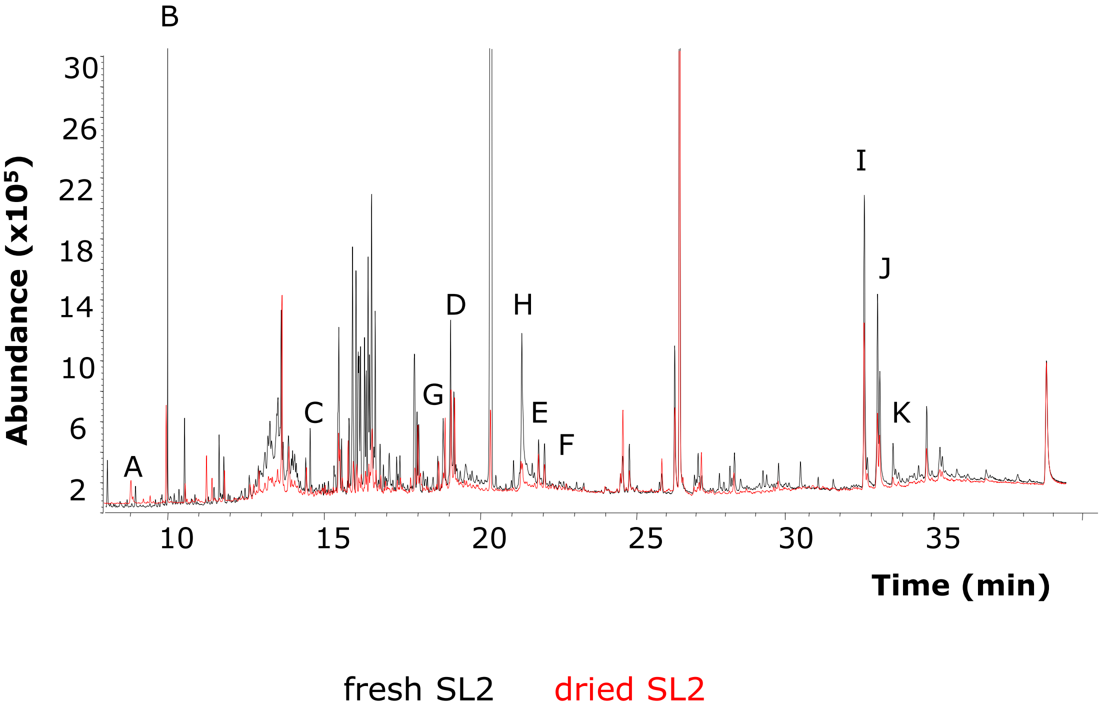

Figure 3.5. Full scan chromatograms of leachates obtained from fresh and dried SL2 sludge samples (identified compounds are listed in Table 3.4)

Table 3.6. Identified compounds in sludge leachates obtained from fresh and dried sludge samples

	Compound	**t_R (min)**	**$\log K_{OW}$**	**Sludge**	**SL1**	**SL2**	**SL3**	**SL4**	**SL5**
	Aromatic alcohols								
A	Benzenepropanol	8.8	2.48	fresh	++	nd	++	+	nd
	[000122-97-4]*			dried	+	nd	+	nd	nd
B	Indole	10.0	2.14	fresh	++	++	++	++	++
	[000120-72-9]*			dried	++	+	++	+	+
	Aliphatic carboxylic acids								
C	Dodecanoic acid	14.0	4.09	fresh	++	+	++	++	++
	[000143-07-7]*			dried	+	+	++	+	++
D	n-Hexadecanoic acid	19.0	6.75	fresh	++	+	++	++	++
	[000057-10-3]*			dried	+	+	++	+	++
E	trans-13-dodecanoic acid	21.8	7.26	fresh	++	++	++	++	nd
	[000693-71-0]*			dried	+	+	+	nd	++
F	Oleic acid	21.9	7.64	fresh	++	+	++	++	++
	[000112-80-1]*			dried	+	nd	++	+	++
	Polycyclic aromatic compounds								
G	Galaxolide-1	18.3	5.90	fresh	++	+	++	nd	nd
	[1000285-26-6]*			dried	+	+	+	nd	nd
	Sulphur compounds								
H	Cyclic octaatomic sulphur	21.0	0.23	fresh	++	++	++	++	++
	[010544-50- 0]*			dried	++	+	+	nd	++
	Sterols								
I	Cholestan-3-ol	33.2	8.80	fresh	++	++	++	+	++
	[000360-68-9]*			dried	+	++	++	+	+
J	Cholestan-3-one	33.6	8.31	fresh	++	++	++	nd	nd
	[000601-53-6]*			dried	nd	+	++	nd	nd
K	Cholestanol	34.0	8.82	fresh	++	++	nd	nd	nd
	[000080-97-7]*			dried	+	+	nd	nd	nd

* Corresponding CAS number of compound identified
+ peak abundance $< 10^6$
++ peak abundance $> 10^6$
nd - not detected

3.3.1.2. Leaching of heavy metals from sludge

The concentrations of heavy metals in sludge leachates are presented in Table 3.7, whereas Figure 3.6 compares the leaching yields of heavy metals from fresh and dried samples.

Table 3.7. Concentration of heavy metals (Value (SD); n = 3) in leachates obtained from fresh and dried sludge samples (mg kg^{-1})

Heavy metal	**Sludge**	**SL1**	**SL2**	**SL3**	**SL4**	**SL5**
Cu	Fresh	0.9 (0.1)	5 (1)	1.9 (0.2)	0.2 (0.2)	0.3 (0.2)
	Dried	10 (2)	5 (1)	10 (7)	73 (14)	4 (2)
Ni	Fresh	2.9 (0.1)	3.3 (0.3)	2.8 (0.1)	0.6 (0.1)	1.3 (0.2)
	Dried	20 (1)	5.7 (0.3)	16 (1)	4.7 (0.2)	6.9 (0.1)
Pb	Fresh	0.5 (0.1)	0.3 (0.1)	0.7 (0.5)	0.5 (0.1)	0.7 (0.2)
	Dried	0.6 (0.1)	0.5 (0.1)	0.16 (0.01)	0.15 (0.05)	0.8 (0.3)
Zn	Fresh	6.1 (0.3)	20 (10)	6.3 (0.5)	5 (1)	11.5 (0.3)
	Dried	3.5 (0.1)	8 (2)	8 (5)	6 (1)	19 (1)
Cr	Fresh	0.9 (0.1)	1.3 (0.5)	0.9 (0.2)	0.9 (0.1)	1.1 (0.1)
	Dried	0.6 (0.1)	0.5 (0.1)	0.8 (0.4)	0.5 (0.1)	1.0 (0.1)

Nickel showed the highest leaching rates, with values for fresh and dried sludge samples up to 13.1 and 43.4%, respectively. These relatively high values are in good agreement with the leaching rates previously reported for this metal in sludge samples, and it is consistent with its relatively high mobility in environmental samples (Wong et al., 2001). Nickel was leached in higher percentages from dried sludge samples. This pattern can be partially explained by the lower pH values of dried sludge sample leachates. As noted in previous studies, the affinity metal-organic matter decreases at lower pH values (Fuentes et al., 2004; Ashworth and Alloway, 2008). Moreover, the DOC content was much higher in dried samples, thus contributing to the solubilisation of this metal (Liu et al., 2007). The role of the organic matter in the Ni leaching rate was supported by the fact that the variation in DOC explains a large amount of the leaching rate variability for Ni in dried sludge samples ($R^2 = 0.44$).

Copper showed the lowest leaching rates from fresh sludge samples (< 0.4%). Although Cu had much lower leaching rates than Ni, its leaching pattern was comparable to that of Ni, as Cu leaching was higher from dried sludge samples (with the highest value of 11.6% for SL4) than for fresh sludge samples. The similarity can also be explained by the affinity of Cu for organic matter (Dijkstra et al., 2004), as the formation of soluble complex between Cu and DOC facilitates metal remobilisation (Bolan et al., 2003).

The leachability of Pb, Zn and Cr was generally very low in both fresh and dried samples (below 5%). Although dried SL5, with the lowest pH and the highest DOC, had Pb and Zn leached at higher rates than in the analogous fresh sample, there was no consistent correlation between the type of sludge (fresh or dried) and the leaching yields, and differences between leaching rates from fresh and dried sludge samples were not statistically significant in most cases. The low leaching rates of the metals agree with reported data that show the negligible leachability of Pb and Zn in sludge samples across the pH values tested in this study (Wong et al., 2001; García-Delgado et al., 2007).

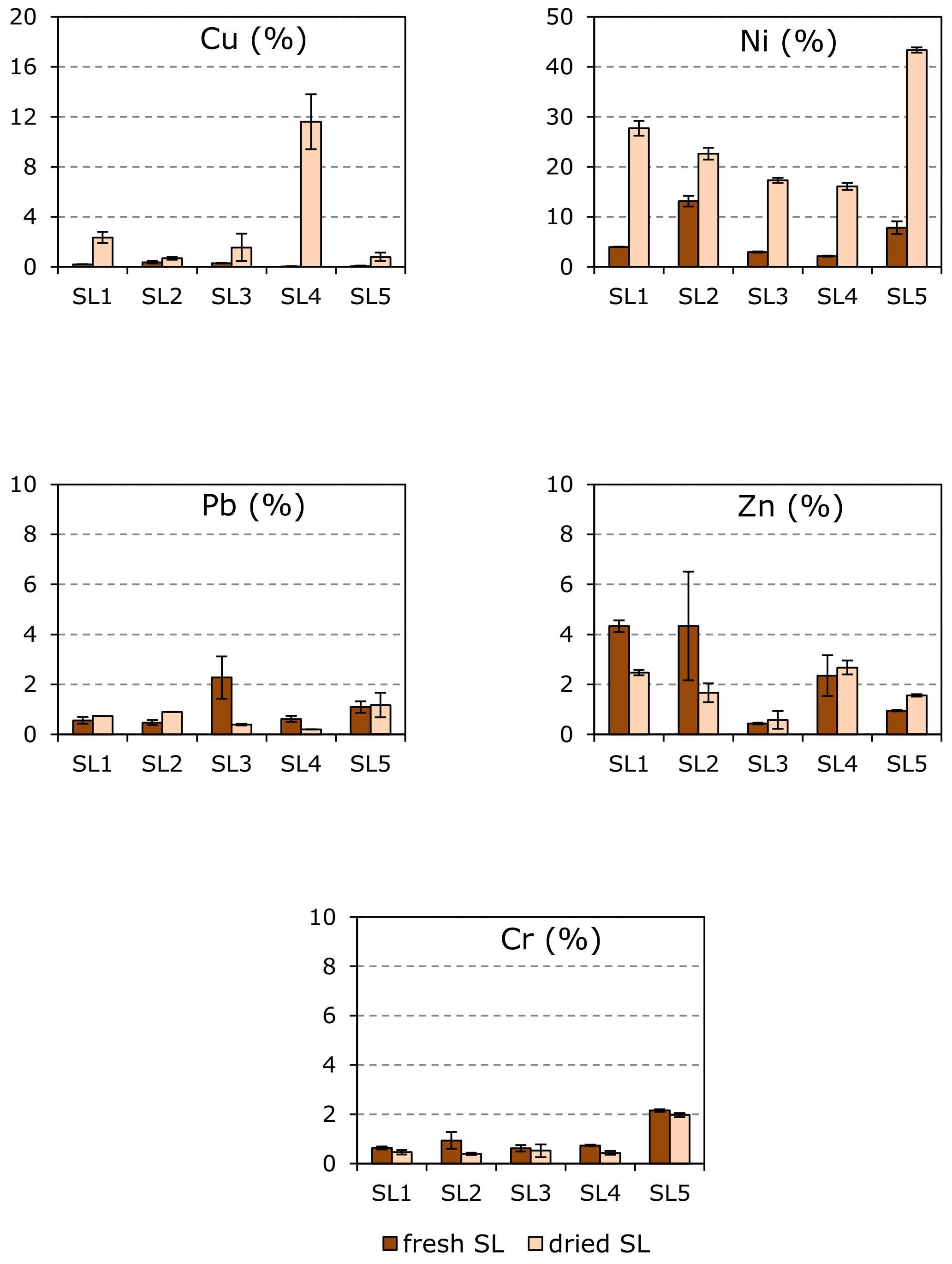

Figure 3.6. Leaching yields of heavy metals from fresh and dried sludge samples

3.3.1.3. Leaching of alkylphenolic compounds

The concentrations of OP, NP and NP_1EO in the leachates of both fresh and dried sludge samples are shown in Table 3.8.

The concentrations of OP, NP and NP_1EO in the leachates of the sludge samples ranged over three orders of magnitude. The highest concentrations were found in leachates of fresh sludge samples, with maximum concentrations of 7 mg kg^{-1} for OP (SL1), 19.3 mg kg^{-1} for NP (SL3) and 1.0 mg kg^{-1} for NP_1EO (SL5).

Figure 3.7 shows the leaching yields of the APCs in fresh and dried samples. Comparing the leaching rates in fresh sewage sludge samples, OP and NP showed the same leaching pattern, with high leaching rates (up to 35% of the total amount present in the sludge) in samples SL1 and SL5 and the lowest leaching rates for the SL4 sample. The highest leaching rates of NP_1EO were obtained in the SL4 and SL5 sludge samples, which had not been subjected to anaerobic digestion, although these rates were still lower than those for OP and NP.

These results confirm that the biological and chemical pre-treatment of sludge in WWTPs significantly affects APC leaching.

The solubility of the APCs (OP (12.6 mg L^{-1}), NP (5.4 mg L^{-1}) and NP_1EO (3.0 mg L^{-1})), which depends on the polar groups that form the hydrophilic part of the APC molecule (Ahel and Giger, 1993b), explained only partially the sequence of APC leaching from sludge samples. On the contrary, the characteristics of the fresh sludge samples, such as the high POC content, explained a significant fraction of the leaching variability of OP, NP and NP_1EO in fresh samples ($R^2 = 0.55$; $R^2 = 0.79$; $R^2 = 0.30$, respectively).

Table 3.8. Concentration of alkylphenolic compounds (Value (SD); n = 3) in leachates obtained from fresh and dried sludge samples (mg kg^{-1})

APC	Sludge	SL1	SL2	SL3	SL4	SL5
OP	Fresh	7 (1)	0.15 (0.05)	0.144 (0.004)	0.006 (0.001)	0.09 (0.01)
	Dried	0.36 (0.03)	0.021 (0.001)	0.015 (0.001)	0.01 (0.01)	0.01 (0.01)
NP	Fresh	7 (2)	6 (2)	19.3 (0.3)	0.15 (0.02)	2.6 (0.3)
	Dried	0.27 (0.01)	0.75 (0.03)	1.9 (0.1)	0.07 (0.04)	0.3 (0.1)
NP_1EO	Fresh	0.3 (0.1)	0.3 (0.1)	0.94 (0.04)	0.20 (0.01)	1.0 (0.1)
	Dried	0.11 (0.02)	0.18 (0.02)	0.59 (0.03)	< 0.05	0.37 (0.02)

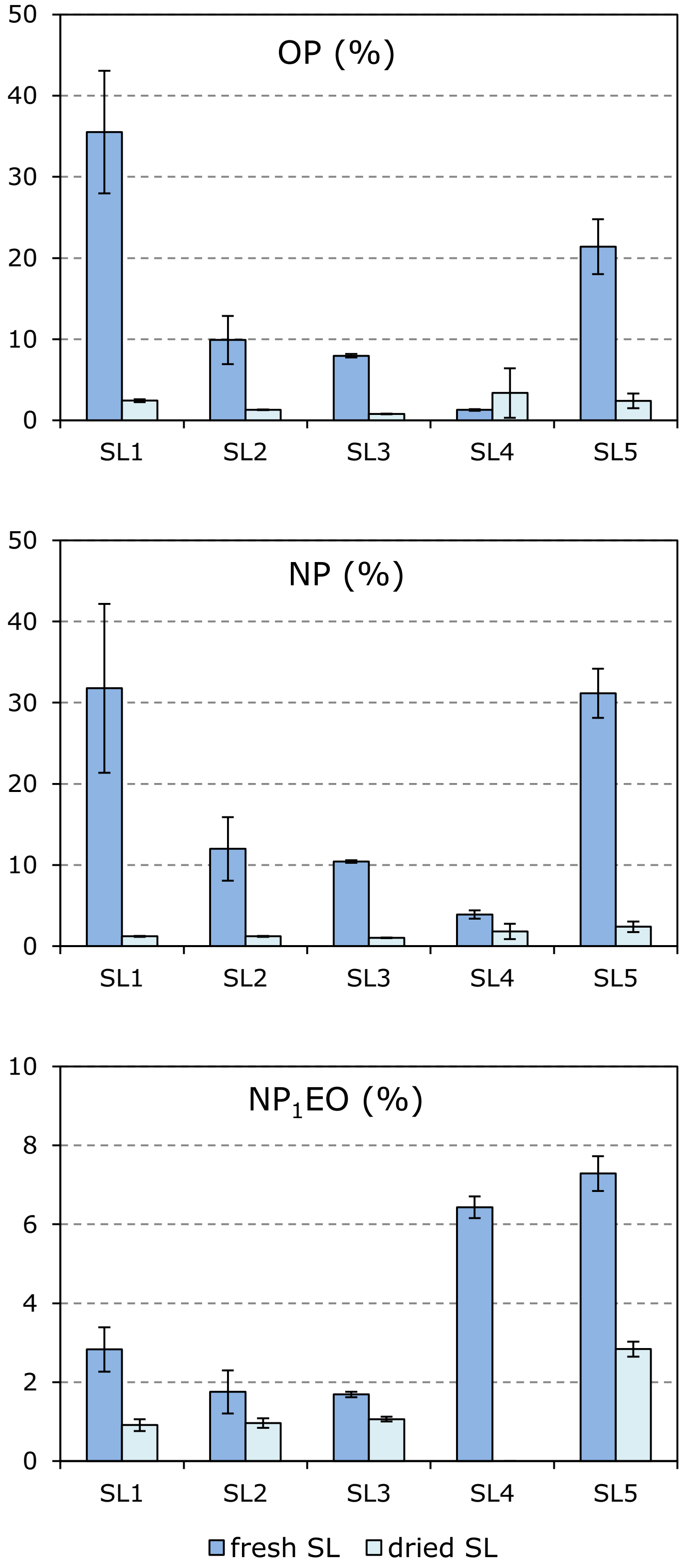

Figure 3.7. Leaching yields of OP, NP and NP_1EO from fresh and dried sludge samples

In the dried sludge samples, as shown in Figure 3.7, the leaching of APCs decreased drastically to values always lower than 3%, and it was very similar among compounds and samples of different origin. APC leaching rates were significantly affected by changes in pH, DOC and TOC. For instance, the variability of pH explained satisfactorily the variation in the leaching rates of OP, NP and NP_1EO (R^2 =0.47; R^2 =0.86; R^2 =0.89, respectively); whereas changes in TOC also explained a large amount of the variation in the leaching rates of OP, NP and NP_1EO (R^2 =0.34; R^2 =0.98; R^2 =0.98, respectively).

Therefore, the decrease in the leachability of APCs observed in dried sludge samples might be attributed to the fact that these compounds are associated with particulate organic matter present in the leachate of fresh samples and thus are easily extracted. In contrast, in the dried sludge samples, the amount of POC is considerably reduced and APCs remain in the solid phase of the sludge, their leachability in water decreasing drastically.

3.3.2. Sorption behaviour of nonylphenol and nonylphenol-mono-ethoxylate in soils

3.3.2.1. Sorption isotherms of NP and NP_1EO

The sorption isotherms of NP and NP_1EO in the five soils analysed are shown in Figures 3.8 and 3.9, respectively. Regarding NP, the C_s *vs.* C_{eq} plots followed a linear pattern, as confirmed by the N parameter of the Freundlich model, which approached to 1 (Table 3.9). Linearity of sorption isotherms agreed with previously reported results for NP (Düring et al., 2002).

According to some authors (Karickhoff, 1981) sorption linearity can be explained by the low C_{eq} concentration values of APCs, which were below one half of the solubility in water of either NP (5.4 mg L^{-1}) or NP_1EO (3.0 mg L^{-1}) (Ahel and Giger, 1993b). Moreover, sorption for nonpolar hydrophobic compounds, such as NP, is based predominantly on Van der Waals interactions between solute molecules and soil organic matter (Karickhoff, 1981). The contribution to the sorption of the deprotonated species was negligible because of the pH of the samples, which was much lower than the assumed pK_a of NP (10.7) (Duhalt et al., 2005).

The K_d values obtained from the slope of linear isotherms for the soils (ranging from 24 to 1059 mL g^{-1}) were similar to the K_F values (ranging from 29 to 1160 mL g^{-1}), as both parameters were highly correlated ($K_F = 1.1 (0.1) \cdot K_d$; $R^2 = 0.99$), thus confirming that both models were suitable to describe NP sorption in soils. Both parameters varied in a broad range of almost two orders of magnitude, between the lowest value for ASCO and the highest for OVI01, in a sequence of increasing values consistent with the increase in the OC content. This relationship is further discussed in a section below.

Concerning NP_1EO, whereas a similar sorption pattern could be generally observed, the sorption of this APC in ASCO and OVI01 soils was not linear for the entire range of initial concentrations (Figure 3.9).

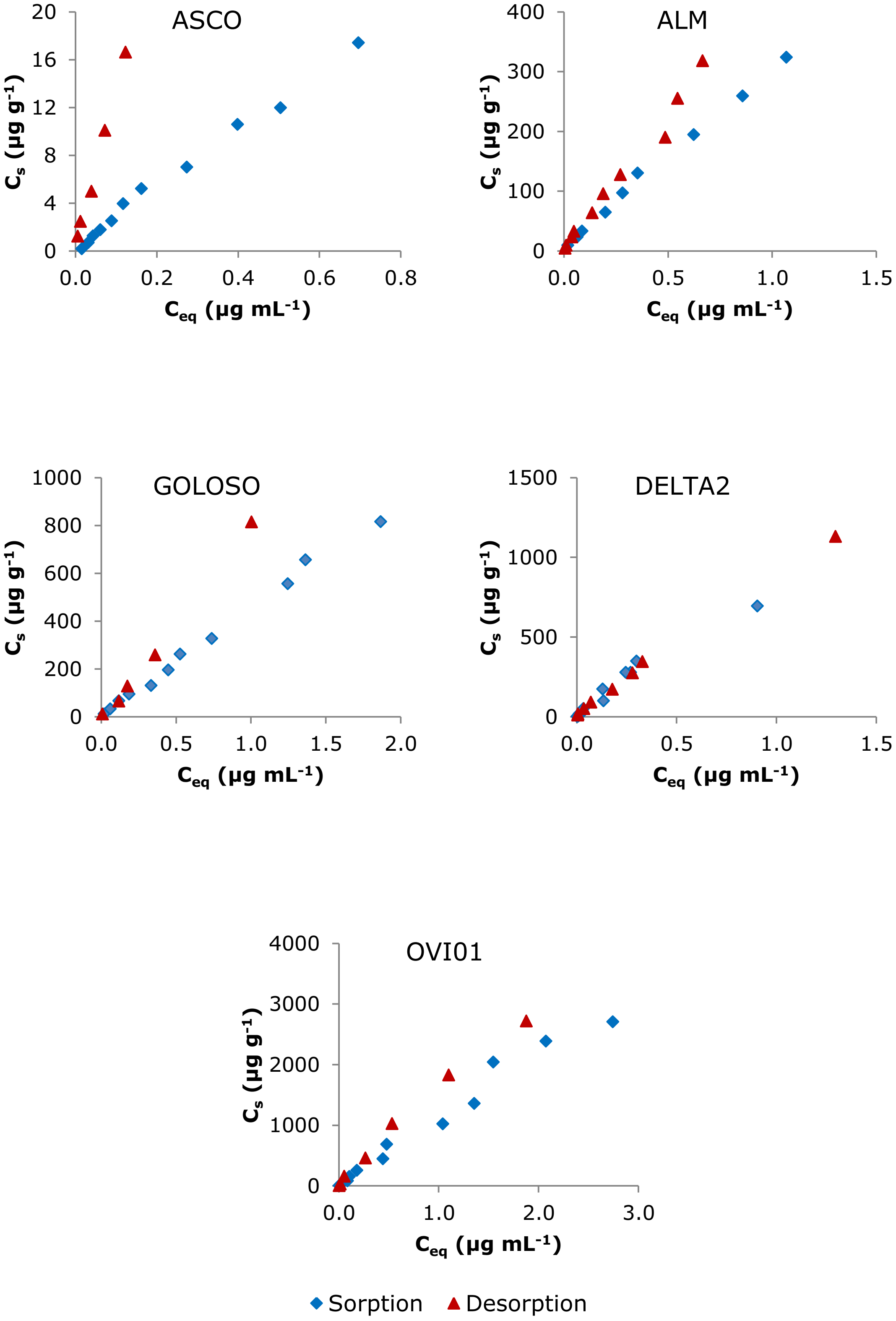

Figure 3.8. Sorption and desorption isotherms of NP in the analysed soils

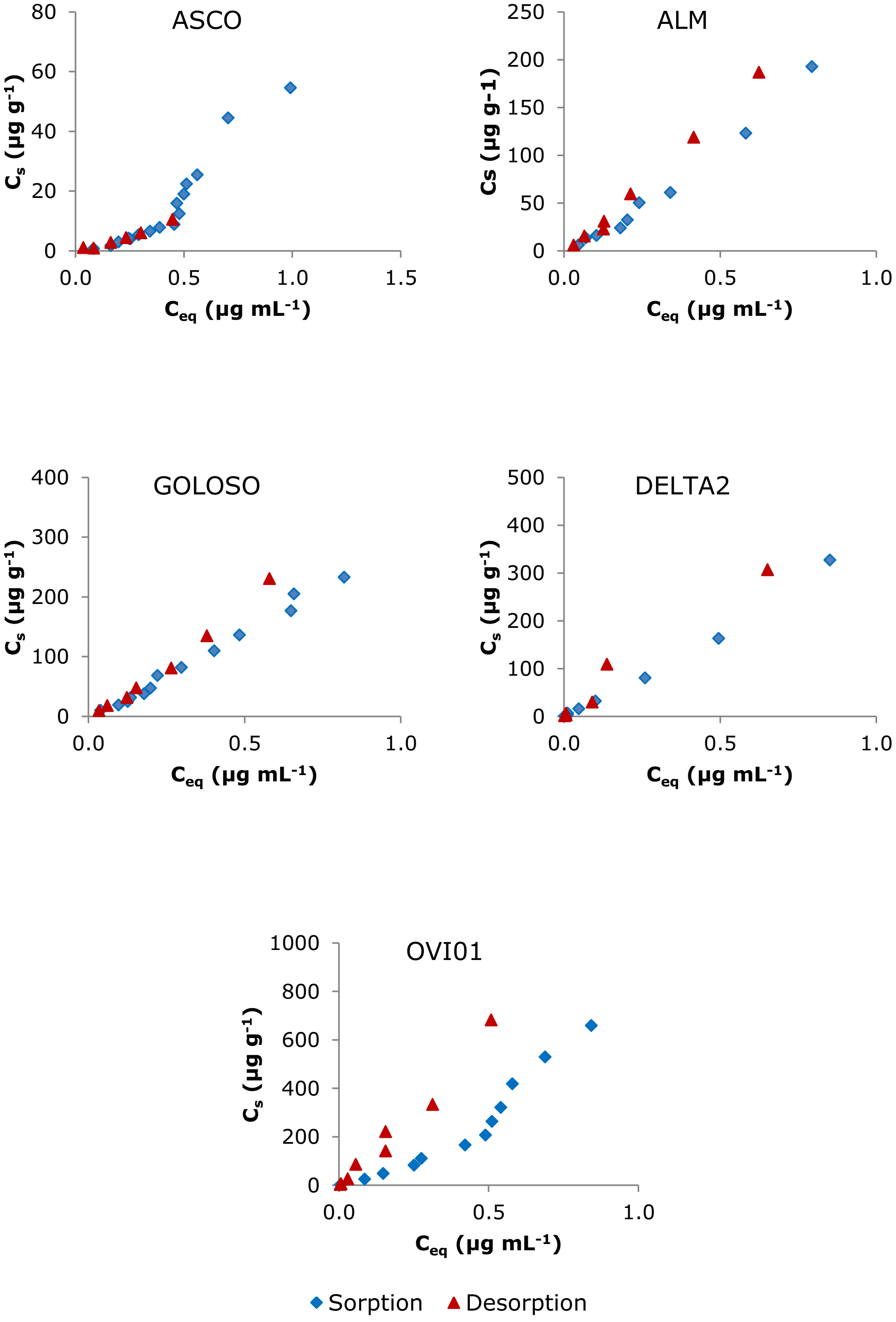

Figure 3.9. Sorption and desorption isotherms of NP_1EO in the analysed soils

Table 3.9. Fitting parameters (value (SD)) obtained from the Freundlich and linear model for sorption and desorption isotherms of NP and NP_1EO in soils

APC	Soil	Sorption			Desorption		
		Freundlich model		**Linear model**	**Freundlich model**		**Linear model**
		N	**K_F (g^{1-N} mL^N g^{-1})**	**K_d (mL g^{-1})**	**N_{des}**	**$K_{F,des}$ (g^{1-Ndes} mL^{Ndes} g^{-1})**	**$K_{d,des}$ (mL g^{-1})**
NP	**ASCO**	1.0 (0.1)	29 (2)	24 (1)	0.9 (0.1)	81 (20)	130 (4)
	ALM	0.9 (0.1)	299 (4)	297 (7)	0.9 (0.1)	402 (27)	446 (18)
	GOLOSO	0.9 (0.1)	451 (10)	446 (10)	0.9 (0.2)	671 (85)	821 (25)
	DELTA2	0.8 (0.1)	764 (31)	795 (53)	0.9 (0.1)	802 (46)	862 (17)
	OVI01	0.9 (0.1)	1160 (67)	1059 (47)	0.9 (0.1)	1760 (118)	1467 (69)
NP_1EO	**ASCO**	1.7 (0.2)	60 (4)	23* (1) 79** (11)	0.9 (0.2)	18 (5)	24 (2)
	ALM	1.1 (0.1)	228 (12)	244 (12)	1.1 (0.1)	322 (11)	309 (9)
	GOLOSO	1.1 (0.1)	296 (9)	299 (9)	1.1 (0.1)	386 (32)	403 (20)
	DELTA2	1.0 (0.1)	337 (19)	371 (11)	0.9 (0.2)	519 (64)	470 (39)
	OVI01	1.8 (0.1)	929 (60)	425* (21) 1055** (142)	1.1 (0.1)	1470 (179)	1285 (83)

For equilibrium concentrations lower than 0.5 µg mL^{-1} the NP$_1$EO sorption pattern was linear with an almost constant solid-liquid distribution coefficient, but for equilibrium concentrations higher than 0.5 µg mL^{-1} an increase in the slope was noticed. This was confirmed by the Freundlich fitting, as the N parameter for these soils had values higher than 1 (N = 1.7 in ASCO and 1.8 in OVI1) (Table 3.9). Two explanations can be found for N > 1 values: solute-solute interactions through vertical packing of alkyl chains, which may cause cooperative sorption; or solute sorption inhibited, at low solute concentrations, by a competing reaction within the solution, such as interaction with DOC (Giles et al., 1974). Taking into account that this sorption pattern with N > 1 was only observed for NP$_1$EO in the two soils with a higher DOC/OC ratio (ASCO and OVI01), and the more polar nature of NP$_1$EO (log K$_{OW}$ 4.2) with respect to NP (log K$_{OW}$ 4.5) (Ahel and Giger, 1993a), it is possible to hypothesize that at low concentrations of NP$_1$EO (C$_{eq}$ < 0.5 µg mL^{-1}) there is a competition between DOC in the liquid phase and OC in the solid phase for the sorption of the compound. This fact would lead to lower K$_d$ values than expected at low concentrations of NP$_1$EO, whereas at higher concentrations, the OC in the solid phase might control NP$_1$EO sorption. On the contrary, the solute-solute interaction can be considered not significant, because this behaviour was not observed in the rest of soils.

For those cases for which a linear model was suitable, the K$_F$ and K$_d$ values for NP$_1$EO were similar, and generally lower than the respective values for NP. This might be also explained by the more polar nature of NP$_1$EO with respect to NP, and was in agreement with previously reported data of comparable environmental matrices, such as suspended particulate matter (Hou et al., 2006). As a single linear model could not be applied for all the concentration ranges for NP$_1$EO in the ASCO and OVI01 soils, linear K$_d$ values were deduced from the slope of two zones: for low (C$_{eq}$ < 0.5 µg mL^{-1}) and high (C$_{eq}$ > 0.5 µg mL^{-1}) concentration ranges (Table 3.9). However, the mean of the two K$_d$ values, at low and high concentrations, was considered for comparison purposes, i.e., 51 for ASCO and 740 mg L^{-1} for OVI01.

3.3.2.2. Desorption isotherms of NP and NP_1EO

Desorption isotherms of NP and NP_1EO in soils are also shown in Figures 3.8 and 3.9, respectively. Isotherms followed a linear pattern for both APCs, which was confirmed by the values of the N parameter derived from the fitting with the Freundlich equation (Table 3.9). $K_{F,des}$ and $K_{d,des}$ parameters followed a two-order of magnitude increase from ASCO to OVI01 soils similar to that observed for the sorption data. Both parameters were correlated for both APCs (NP: $K_{F,des} = 1.4 (0.2) \cdot K_{d,des}$, $R^2 = 0.96$; NP_1EO: $K_{F,des} = 1.19 (0.04) \cdot K_{d,des}$; $R^2 = 0.998$), thus indicating that the two models were suitable to describe the desorption isotherms. As observed in the previous sorption stage, the desorption parameters were higher for NP than for NP_1EO. Comparing desorption and sorption parameters, $K_{F,des}$ and $K_{d,des}$ were generally higher than K_F and K_d, respectively (with the exception of the $K_{F,des}$ and K_F of NP_1EO in ASCO) and were correlated to the sorption parameters (NP: $K_{F,des} = 1.5 (0.3) \cdot K_F$, $R^2 = 0.92$; $K_{d,des} = 1.1 (0.3) \cdot K_d$, $R^2 = 0.85$; NP_1EO: $K_{F,des} = 2.9 (0.2) \cdot K_F$, $R^2 = 0.99$; $K_{d,des} = 2.0 (0.1) \cdot K_d$, $R^2 = 0.99$). This indicated that desorption parameters were significantly higher and that the sorption was partially irreversible. Therefore hysteresis was a significant process related to the sorption of NP and NP_1EO in soils.

Desorption yields of target APCs, were lower than 5% for all the APC-soil combinations, thus ensuring that NP and NP_1EO sorption was highly irreversible. The exception of this pattern was the sorption of NP_1EO in the ASCO sample, with a desorption yield of around 45%, which agreed with its low $K_{d,des}$ (the lowest among all the APC-soil combinations investigated).

3.3.2.3. Correlation of K_d with physicochemical properties of APCs and soil characteristics

As the OC played a major role in the variation of the sorption and desorption parameters of NP and NP_1EO in the soils investigated, the relationship between the K_d and the fraction of organic carbon in soil was further explored. As suggested by Karickhoff (1981) the sorbed concentration of a compound in a sorbent mixture can be taken as a weighted sum of the sorption at the different site pools:

$$C_s = \sum_i C_{s,i} \, F_i \tag{3.11}$$

where F_i would denote the specific weight of each site pool (expressed as gram of the site pool per gram of soil) and $C_{s,i}$ is the concentration of compound sorbed at each site pool (expressed as µg of compound per gram of site pool). Dividing Eq. 3.11 by the concentration of compound in the aqueous phase in equilibrium, C_{eq}, the following expression can be derived:

$$\sum_i \frac{C_{s,i}}{C_{eq}} F_i = \sum_i K_i \, F_i = \sum_i K_{d,i} = K_d \tag{3.12}$$

where K_i is the solid-liquid distribution coefficient of the compound at each site pool referred to its weight, $K_{d,i}$ is the solid-liquid distribution coefficient of the compound at each site pool referred to the total weight of the sorbent, and K_d is the global solid-liquid distribution coefficient of the compound in the sorbent mixture.

In a simplistic approach, a soil may be considered as a mixture of two main site pools, the organic and mineral fractions. Thus, the solid-liquid distribution coefficient of a compound in a soil can be expressed as:

$$K_d = K_{d,ORG} + K_{d,MIN} = K_{OC} \cdot F_{OC} + K_{d,MIN} \tag{3.13}$$

where K_{OC} is the sorption solid-liquid distribution coefficient of the compound referred to the weight of organic carbon in soil, and F_{OC} are the grams of organic carbon per gram of soil. Therefore, a K_{OC} value for a given compound can be derived from the slope of the K_d *vs.* F_{OC} correlation obtained in various soils. Figure 3.10 plots the correlations obtained for the two APCs investigated in this work. The strong dependence between the K_d values and the soil organic carbon for NP and NP_1EO (R^2 = 0.98 and 0.83, respectively) allowed us to deduce K_{OC}

values from the slope of the curves, showing that NP (K_{OC} = 10320 (830) mL g^{-1}) was less mobile than NP_1EO (K_{OC} = 5860 (1540) mL g^{-1}).

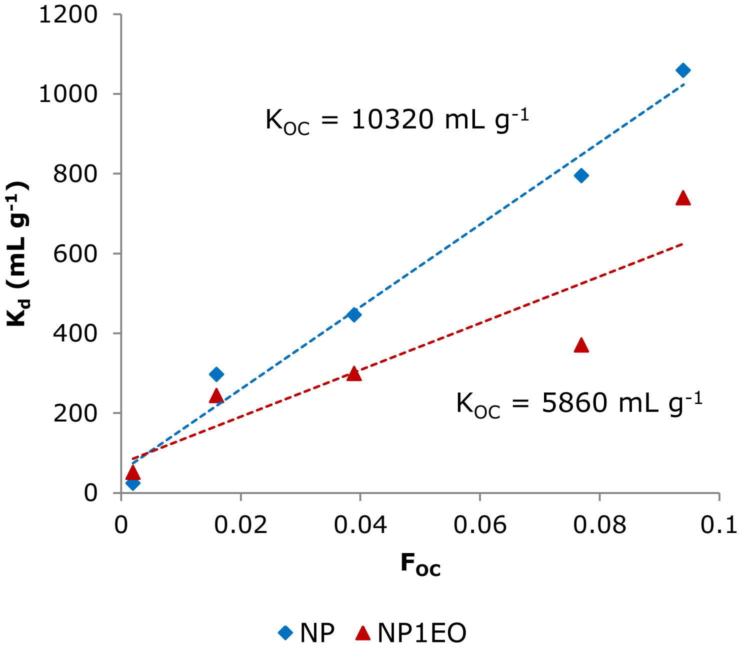

Figure 3.10. Correlation between K_d and organic carbon fraction for NP and NP_1EO in the analysed soils

The values for the intercepts ($K_{d,MIN}$) were not statistically different to zero, thus indicating the negligible role of the soil mineral fraction in the sorption pattern of both compounds. This was consistent with the proposed sorption mechanism.

The deduced log K_{OC} value for NP (4.0) was similar to reported values originated from similar experiments (Düring et al., 2002; Höllrigl-Rosta et al., 2003), but lower than the reported value of 4.9 (Ying and Kookana, 2005), probably due to the different conditions used in the sorption test (e.g. different composition of the aqueous solution and much shorter equilibration time). The log K_{OC} for NP_1EO (3.8) cannot be compared with previous results, due to the lack of available information on this APC.

Apart from the K_d *vs.* F_{OC} correlation approach, the K_{OC} values can also be estimated from empirical correlations that make use of the octanol-water partition coefficient, K_{OW}, and that vary according to solute. Table 3.10 summarizes some of the more relevant empirical correlations found in the literature for non-ionic and hydrophobic organic compounds, as well as their range of application as a function of K_{OW} values.

Table 3.10. Empirical correlations between log K_{OC} and log K_{OW}

Empirical correlation	**Range of application**		**Derived log K_{OC}**	
	log K_{OW}	**Sorbent**	**NP (log K_{OW} 4.5)**	**NP_1EO (log K_{OW} 4.2)**
log K_{OC} = 0.9 log K_{OW} - 0.5 Chiou et al. (1983)	2.1 - 5.6	Soils	3.5	3.2
log K_{OC} = log K_{OW} - 0.2 Karickhoff (1981)	2.1 - 6.3	Soils and sediments	4.1	3.8
log K_{OC} = 0.6 log K_{OW} + 0.9 Sabljic et al. (1995)	1 - 5	Soils	3.7	3.5

From log K_{OW} values for NP (4.5) and NP_1EO (4.2) (Ahel and Giger, 1993a), the log K_{OC} for NP and NP_1EO were calculated by using the different correlations, as shown in Table 3.10. Values obtained in this work were extremely similar to those predicted from the Karickhoff correlation (1981) and slightly higher than those calculated by the other two correlations. These results confirmed the robustness of the log K_{OC} data obtained in the present work and suggested that the interaction of APCs with the organic matter fraction of soils depends basically on the K_{OW} value of the compound.

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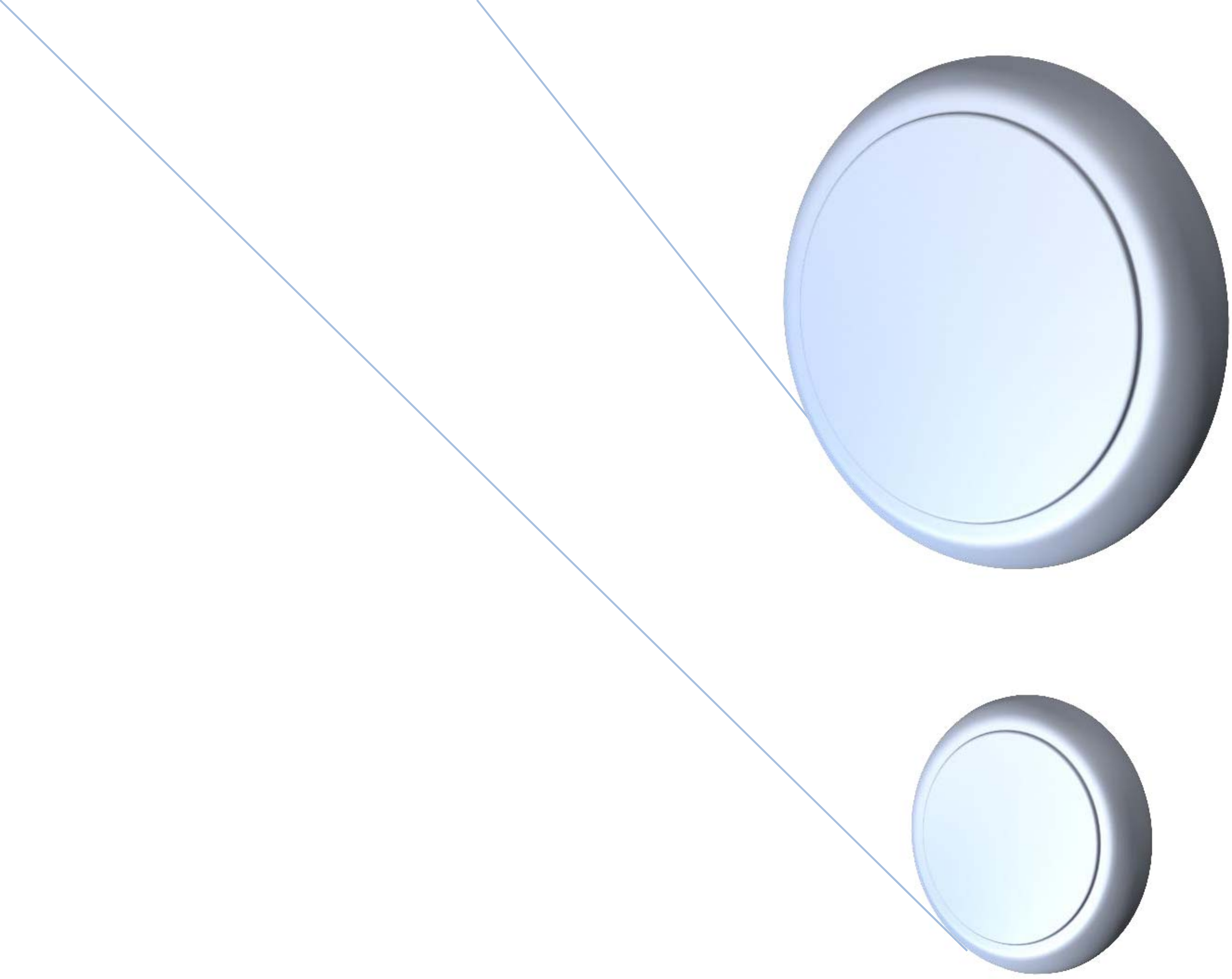


Chapter 4. Interaction of perfluorinated compounds with sewage sludges and soils

4.1. Introduction

Perfluorinated compounds are surface active compounds, characterized by a fully fluorinated hydrophobic alkyl chain of varying length, attached to different hydrophilic groups, such as sulfonate or carboxyl (Section 2.4.2.1). Strong C-F bonds make PFCs extremely resistant to hydrolysis and to thermal, microbiological and photolytic degradation. As a consequence, they are ubiquitous in diverse environmental matrices, including water (Taniyasu et al., 2003; Ahrens et al., 2009), sewage sludge (Yoo et al., 2009; Sun et al., 2011), soils (Strynar et al., 2012; Wang et al., 2013) and sediments (Bao et al., 2010; Yang et al., 2011).

Among all PFCs, perfluorooctane sulfonate (PFOS), and perfluorooctanoic acid (PFOA) are those that show a higher accumulation in the environment (Ellis et al., 2004), due to their long chain. These compounds have been directly released or generated by the microbial degradation of other PFCs (Paul et al., 2009). In 2009, PFOS and its salts were added to the list of persistent organic pollutants of the Stockholm Convention and hence their production and use in most application areas were prohibited in the EU (UNEP, 2009). Recently, the perfluorobutane sulfonate (PFBS) has been commercialised as a homologous compound of PFOS in a variety of applications (OECD, 2006). PFBS has a four carbon-chain with a sulfonate hydrophilic group, which makes it less bioaccumulative compared to PFOS (Newsted et al., 2008).

PFCs have been detected in wastewaters and in different products of their treatment in wastewater treatment plants (WWTPs). This indicates that wastewater treatments cannot completely degrade PFCs, and thus a significant fraction can be found in resulting sewage sludge (Sinclair and Kannan, 2006; Busch et al., 2010; Llorca et al., 2011). PFOS and PFOA were found in sludge samples from Denmark, Spain, Switzerland and USA in the ng g^{-1} range, whereas higher concentrations (up to µg g^{-1}) were found in samples from China and Germany (Sun et al., 2011).

Not only the total amount of PFCs, but also their sorption pattern in sludge is of great importance to evaluate the environmental risk associated with these organic pollutants. Sorption data of PFCs in sludges has been scarcely reported to date. Results indicated that sorption solid-liquid distribution coefficients (K_d) may range within up to three orders of magnitude, depending on PFCs physicochemical characteristics, sludge properties (digestion treatment) and concentrations of PFCs in wastewaters, although sorption mechanisms were not clearly elucidated due to the hydrophobic and hydrophilic nature of the PFCs (Ochoa-Herrera and Sierra-Alvarez, 2008; Zhou et al., 2010; Zhang et al., 2013). Besides the limited information about the sorption of PFCs in sludge, to the best of our knowledge there are no available data about the sorption reversibility of PFCs in sludges, although in situ K_d data with regarding sludge suspended matter and wastewaters in contact, are available (Arvaniti et al., 2012).

Data regarding the concentrations of PFCs in soils are scarce in the literature. PFCs were found at ng g^{-1} levels in ten soil samples from several countries (Japan, Mexico, USA), with the highest concentrations found for PFOS and PFOA, which were 10 and 30 ng g^{-1}, respectively (Strynar et al., 2012). Li et al., (2010) reported similar concentration levels of PFOS and PFOA in soils from Shanghai, in China. However, not only the total amount of PFCs in soils, but also their distribution between the solid phase and the soil solution is of great importance, influencing their environmental fate. To date, the sorption of PFCs in soils has been reported only in a few studies (Johnson et al., 2007; Chen et al., 2009; Enevoldsen and Juhler, 2010; Chen et al., 2013) and it was quantitatively described by sorption parameters, such as the sorption solid-liquid distribution coefficient, K_d. For the same compound, K_d values varied up to two orders of magnitude, suggesting that many factors influenced the sorption pattern of these PFCs in soils, soil organic carbon being the most relevant.

In order to better understand the sorption mechanism of PFCs in sewage sludges and soils, in this Chapter the sorption behaviour of the most environmental relevant PFCs (PFOS, PFOA and PFBS) was evaluated in sewage sludge and soil samples with contrasting properties, such as pH, organic matter content and dissolved organic carbon. Sorption and desorption tests were applied and corresponding isotherms were built up in a wide range of initial concentrations of target compounds. Isotherms were fitted to appropriate sorption models (Freundlich and linear) and sorption behaviour of each compound was quantitatively described by derived fitting parameters. Effects of sludge and soil parameters, as well as of some main physicochemical properties of PFCs, were considered to explain their sorption mechanisms. Furthermore, the sorption reversibility of each compound was determined and compared.

4.2. Materials and methods

4.2.1. Reagents and standards

Milli-Q double deionised water, $CaCl_2 \cdot 2H_2O$ and NaN_3 were purchased as it was described in previous Chapter (Section 3.2.1.). Water, ammonium acetate and acetonitrile, all of them gradient grade for liquid chromatography, were supplied by Merck (Germany). Analytical standards of perfluorooctane sulfonate (PFOS, potassium salt, 98%) and perfluorooctanoic acid (PFOA, 99.2%) were purchased from Sigma-Aldrich (Germany) and perfluorobutane sulfonate (PFBS, tetrabutylammonium salt, 98%) was purchased from Sigma-Aldrich (Switzerland). Main physicochemical properties of PFCs selected for the sorption study are shown in Table 2.5. Among the three PFCs, PFBS presents the highest solubility in water and is more likely to be transported into aqueous environments than PFOA and PFOS, which are less soluble in water. With respect to the octanol-water partition coefficient (K_{OW}) of PFCs, the reported values show a considerable variability, due to the fact that the determination of this parameter for hydrophobic organic compounds is highly operational (Linkov et al., 2005). However, the sequence of values in most works indicates that PFOS is slightly more hydrophobic than PFOA, and PFBS is the most hydrophilic. Here, the values of log K_{OW} obtained by Deng et al. (2012) are considered for the interpretation of results (Table 2.5). Moreover, the three PFCs have very low pK_a values ($pK_a < 0.14$), and thus all them will be dissociated into anionic species in the soil solution, whose normal pH values are higher than 4.

Stock standard solutions of PFOS, PFOA and PFBS of 1 mg mL^{-1} were prepared individually in acetonitrile. Working solutions of PFCs for sorption and desorption experiments were prepared by appropriate dilution of stock standards in acetonitrile. All solutions were stored at -18 °C in 20 mL glass vials.

Isotopically labelled standard solutions of sodium perfluoro-1-[1,2,3,4,-$^{13}C_4$]-octane sulfonate (MPFOS) and perfluoro-n-[1,2,3,4,-$^{13}C_4$]-octanoic acid (MPFOA), both at concentrations of 50 μg mL^{-1}, were purchased from Wellington Laboratories (Canada). Working solutions of MPFOS and MPFOA were prepared by 50 times dilution of standard solutions in acetonitrile. The solutions were stored at -18 °C in chromatographic vials of 2 mL (Waters, USA).

4.2.2. Sample collection and characterisation

4.2.2.1. Sewage sludge samples

Four sewage sludge samples (SL1, SL3, SL4 and SL5) collected in WWTPs located in industrial zones in Catalonia, Spain were transported and stored as previously described (Section 3.2.2.1). For the purposes of this research, sewage sludge samples dried at 40 °C were used.

In addition to the main physicochemical parameters earlier described (Section 3.2.2.1), and the content of heavy metals extractable in aqua regia (Table 3.1) here the content of metals, such as Ca and Mg was determined in the sludge solutions obtained by mixing of sludge with Milli-Q water in a ratio of S/L = 1:10. The total content of Ca and Mg was determined by ICP-OES (Perkin-Elmer, Optima 3200RL) equipped with Perkin-Elmer AS-90 Plus auto sampler. This equipment contains a source of radiofrequency (working at 1150 W and a frequency of 40 MHz), cross-flow nebulizer and a segmented-array charge coupled device detector. The following emission lines were used for elements determined (nm): Ca - 317.933; Mg - 279.077.

The main properties of the sludge samples are summarised in Table 4.1. As can be seen SL1 and SL3 samples were slightly basic with similar pH, SL4 was neutral, whereas sludge sample SL5 was slightly acid. OM content ranged from 62 to 77%. The lower OM content in SL1 and SL3 samples could be the result of the anaerobic digestion performed in these samples.

Table 4.1. Main sludge properties (mean value (SD); n=3)

SL	**Dry matter (%)**	**pH**	**OM (%)**	**Ca (mmol kg^{-1})**	**Mg (mmol kg^{-1})**	**DOC (mg kg^{-1})**
SL1	21.0 (0.2)	8.3 (0.1)	61.6 (0.1)	31 (3)	32 (3)	35900 (60)
SL3	17.2 (0.1)	8.4 (0.1)	62.5 (0.8)	24 (3)	21 (1)	21400 (400)
SL4	13.9 (0.2)	7.1 (0.1)	73.2 (0.1)	50 (1)	38 (1)	53000 (1100)
SL5	16.1 (0.3)	6.1 (0.1)	77.4 (0.2)	54 (1)	86 (1)	70000 (2400)

The Ca+Mg content in sludge solution was inversely correlated to pH (R^2 = 0.95) and directly correlated to OM (R^2 = 0.85). Whereas the DOC and OM contents were not correlated, the DOC and pH values of sludge samples were inversely correlated (R^2 =0.94), confirming that the increase in the concentration of soluble organic compounds caused a decrease in the pH of the sludge samples.

4.2.2.2. Soil samples

Six soil samples (ASCO, ALM, GOLOSO, DELTA2, OVI01 and DUBLIN), of which five were used in the previous study (Section 3.2.2.2) were considered in this work. Selected soils had contrasted characteristics, especially in relation to the organic matter content. In favour of this, soil DUBLIN was included in this study because of its high content of OC (39%). Like the rest of soils, soil DUBLIN corresponded to the top layer (0 - 10 cm depth), and was air-dried and sieved through a 2 mm mesh. Prior to analysis, samples were homogenised and characterised as previously described (Section 3.2.2.2).

The main physicochemical characteristics of the soils studied here are summarised in the previous Chapter (Table 3.2). Particle size analysis showed that the clay content was higher than 10% in almost all soil samples except for DUBLIN, which can be classified as organic soil with the OC content of 39%.

Whereas the content of organic carbon varied more than two orders of magnitude (from 0.2 in the ASCO soil up to 39% in DUBLIN), the DOC content was very similar in most soils, with a maximum value of 5741 mg kg^{-1} found in OVI01. Ratios of DOC *vs.* OC were also calculated and shown in Table 3.2. The highest DOC/OC ratio was found in the ASCO soil, which had the lowest OC content but the highest pH. Despite the low pH of the OVI01 soil, the OC content was relatively soluble and its DOC/OC ratio was the second among the soils investigated. In contrast, DUBLIN presented the highest content of OC, but one of the lowest DOC values (290 mg kg^{-1}), resulting in extremely low DOC/OC ratio.

4.2.3. Sorption and desorption tests

Similar to previously described sorption and desorption tests applied to soil samples (Section 3.2.4), here three grams (corresponding to dry matter) of sewage sludge or soil sample were suspended in 80 mL polypropylene centrifuge tube with 30 mL of 0.01 mol L^{-1} $CaCl_2$ solution (OECD, 2000). Additionally, 0.03 g of NaN_3 was added as a biodegradation inhibitor. The resulting suspension was end-over-end shaken for 24 hours and then known volumes of the PFOS, PFOA or PFBS working solutions were added to the sludge or soil suspensions to cover a final range of initial concentrations. For the sludge samples, added concentrations of PFCs ranged from 160 to 3920 ng mL^{-1} for PFOS, from 35 to 1040 ng mL^{-1} for PFOA and from 30 to 650 ng mL^{-1} for PFBS in the solutions. In the case of soils the ranges of initial concentrations were from 4.9 to 980 ng mL^{-1} for PFOS, from 1.4 to 310 ng mL^{-1} for PFOA and from 1.3 to 150 ng mL^{-1} for PFBS. Concentration ranges of initial concentrations of PFCs depended on the different physicochemical properties of target compounds and expected sequence of sorption, according to their hydrophobic and hydrophilic properties (Table 2.5). The resulting suspensions were shaken for 24 hours at 60 rpm, then centrifuged for 30 min at 9000 *g* (AJ2-HS, Beckman Coulter, USA) and the supernatants were decanted off. Subsequent desorption experiments were carried out for each compound by drying some of sludge and soil residues (40 °C for 48 h), obtained from selected sorption scenarios. Then, 30 mL of 0.01 mol L^{-1} $CaCl_2$ and 0.03 g of NaN_3 were added to the dried sludge and soil residue and after shaking for 24 h the resulting suspension was centrifuged and the supernatant decanted off, as in the sorption test.

For the quantification of the target PFCs, aliquots of 0.75 mL of supernatants obtained from either sorption or desorption experiments were transferred into chromatographic vials of 2 mL. Then, 0.01 mL of the 1 µg mL^{-1} working solution of the internal standard (MPFOS or MPFOA) and 0.24 mL of acetonitrile were pipetted to a chromatographic vial and analysis of PFCs was performed.

4.2.4. Determination of perfluorinated compounds

The concentrations of PFOS, PFOA and PFBS were determined using liquid chromatography (LC) coupled to tandem mass spectrometry (MS/MS). The system consisted of an Acquity UPLC system (Waters, USA) connected to a Triple Quadruple Detector. An Eclipse XDB-C18 column (150 x 2.1 mm, 5 µm particle size) (Agilent, USA) connected to a C_{18} pre-column was used at a flow rate of 0.3 mL min^{-1}.

Chromatographic separation conditions were adapted from Gómez-Canela et al. (2012). In short, a binary gradient mobile phase consisting of acetonitrile (A) and 3 mmol L^{-1} ammonium acetate (B) was used for analysis. Gradient elution started at 25% of A and 75% of B for 1 min, increased to 85% of A in 5 min, then to 100% of A in 30 s and thus maintained for 30 s. Initial conditions (25% of A and 75% of B) were achieved again in the next 1 min, and the system was stabilized for the following 4 min. The injection volume was 10 µL. The main working parameters for the MS detector were set as follows: capillary voltage of 2.8 kV, cone gas flow of 50 L h^{-1}, desolvation gas flow of 100 L h^{-1}, source temperature of 120 °C, and desolvation temperature of 400 °C. Nitrogen (99.9%) and argon (99.9%) were used as cone and collision gases, respectively. Transitions from precursor to product ions, cone voltage and collision energy of multiple reactions monitoring are summarised in Table 4.2. The dwell time established for each transition was 0.1 s and the interscan delay was set at 10 ms.

Table 4.2. Transition ions and parameters of multiple reaction monitoring of PFCs analysis by LC-MS/MS

PFC	Retention time (min)	Transition ions (m/z)	Cone voltage (V)	Collision energy (eV)
MPFOS	4.5	503 → 80 503 → 99	52	39
PFOS	4.5	499 → 80 499 → 99	50	42
MPFOA	3.5	417 → 372	17	10
PFOA	3.5	413 →169 413 → 369	19	20 11
PFBS	2.7	299 → 80 299 → 99	50	29 26

The analysis of PFCs was performed under negative electrospray ionisation mode, and compounds were identified using their characteristic quantification transitions from precursor to product ions (m/z) and their retention times (Figure 4.1). The most abundant fragmentation ions resulted from the cleavage of the bonds mainly in the perfluorinated chain. Thus, as an example, quantification peak of PFOS at m/z 99 corresponded to the $[FSO_3]^-$ fragment, whereas the main ion of PFOA at m/z 369 was attributed to the $[C_7F_{15}]^-$ chain fragment. The ion at m/z 80 corresponded to the sulfonate ion which was used for the quantification of both PFBS and MPFOS, while MPFOA had characteristic fragment ion at m/z at 372 due to the fragment $[C_4{}^{13}C_3F_{15}]$.

The total analysis time was 12 min (1 min for injection, 7 min for chromatographic separation and 4 min for reconditioning). In the case of PFOS two peaks were observed, the one with a higher retention time (at 4.5 min) being attributed to the most abundant and hydrophobic linear form of the compound and the other (at 4.3 min) to branched isomer form of compound (Langlois and Oehme, 2006). The total concentration of PFOS was calculated considering the sum of two peak areas.

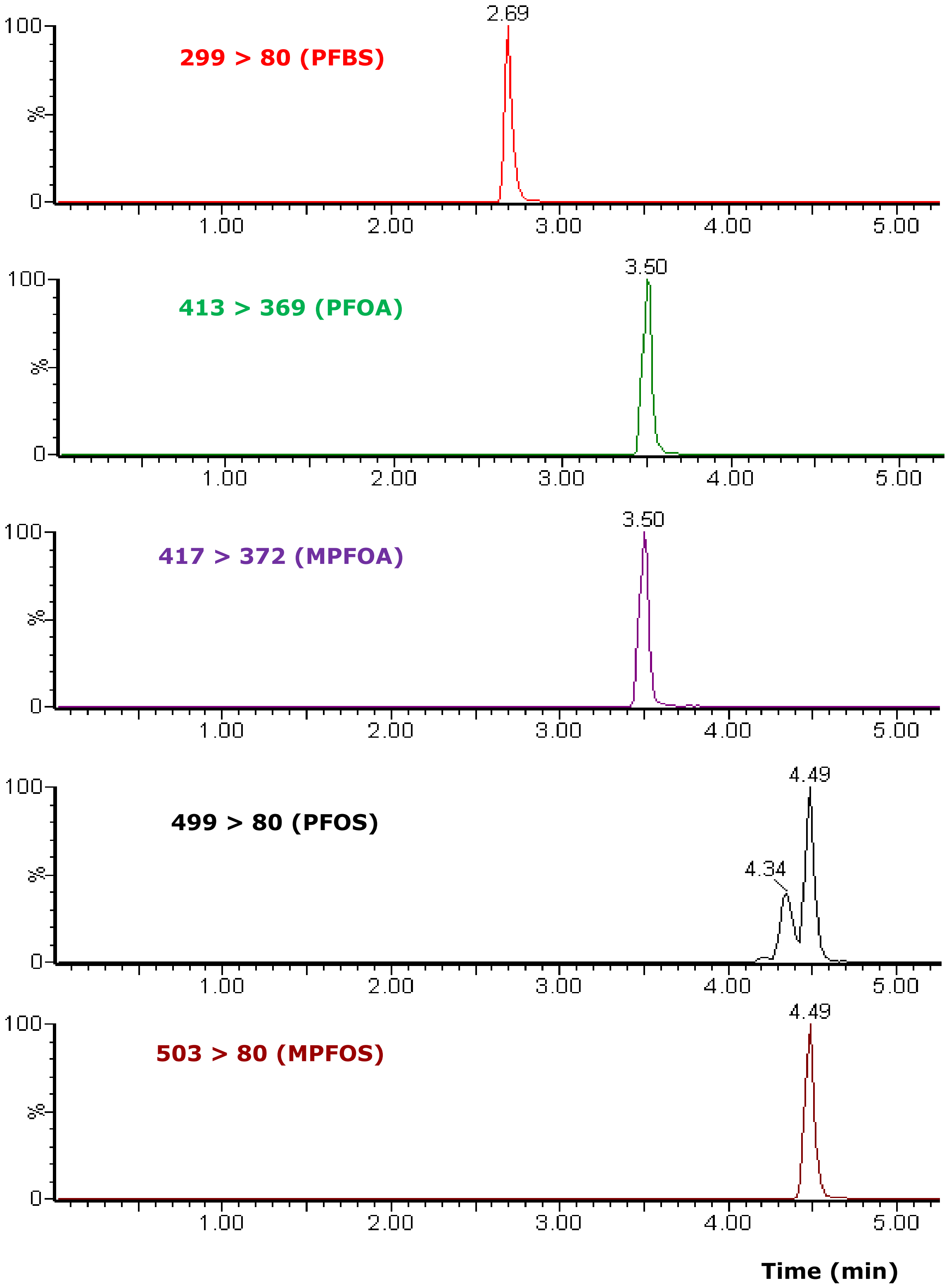


Figure 4.1. LC-MS/MS chromatograms of PFOS, PFOA, PFBS and MPFOS, MPFOA with the respective ion transitions used for quantification and retention times

4.2.4.1. Quality parameters of calibration

Seven point calibration curves were built up over a concentration range from 1 to 300 ng mL^{-1} for PFOS and from 1 to 200 ng mL^{-1} for both PFOA and PFBS. MPFOS was used as an internal standard to quantify PFOS and MPFOA to quantify PFOA and PFBS. The quality parameters of the method, such as slope of the calibration curve and its reproducibility, limits of detection, as well as long term reproducibility, are shown in Table 4.3.

The calibration curves had satisfactory correlation coefficients (R^2 > 0.99) for the three PFCs. As can be seen in Table 4.3, the slightly higher slope of the calibration curve for PFOA indicated a higher sensitivity of LC-MS/MS for the determination of this compound, in comparison with the sulfonated PFCs. The relative standard deviation (RSD) of the slopes was lower than 6% for the three compounds.

Table 4.3. Quality parameters of the calibration of the PFCs analysis

Quality parameter	Sample	PFOS	PFOA	PFBS
Slope (% RSD, n=3)		0.7 (2)	1.0 (4)	0.5 (6)
LOD$_{instr.}$ (ng mL^{-1} in measurement vial)		0.04	0.06	0.05
LOD$_{method}$ (ng mL^{-1} in contact solution)	sludge	0.1	0.1	0.3
	soil	0.2	0.2	0.4
Reproducibility$_{instr.}$ (% RSD, n=5)		3	4	4
Reproducibility$_{method}$ (% RSD, n=3)	sludge	5-17	7-14	8-18

The limit of detection (LOD) was calculated as the concentration of PFC that yielded a signal-to-noise ratio of three (the ratio between the peak intensity and the noise). The instrumental detection limit (LOD$_{instr.}$) was calculated from the chromatogram of the standard solution with the lowest concentration for each compound (1 ng mL^{-1} for three PFCs). The LOD$_{method}$ for the sorption experiment was calculated for all PFCs from the chromatograms corresponding to the contact solutions of the sorption experiments performed with sludge or soil samples. To determine LOD_{method}, two sludge samples (SL4 and SL5) and four soils (GOLOSO and DUBLIN for PFOS; ASCO and ALM for PFOA and the soil OVI01 for PFBS) were used. In Table 4.3, the LOD_{method} is referred to the minimum concentration of PFC that can be detected in the sample contact solution. LOD_{method} values were very similar between the two matrices because of the simplicity of the contact solution obtained in water and the final dilution performed for the analysis in both cases.

Long-term reproducibility of the measurement ($Reproducibility_{instr.}$) was calculated as the relative standard deviation of five determinations, in different days, of a standard solution of 5 ng mL^{-1} of each PFC. The long-term reproducibility of the method ($Reproducibility_{method}$) was calculated as the relative standard deviation of the three analyses performed for each PFC in the sludge samples and is given as a range for each compound (Table 4.3). Reproducibility was reasonable with RSD values between 5 and 18%.

4.2.4.2. Quality control of the analysis

In order to minimize the contamination of samples, polytetrafluoroethylene (Teflon) material was not used in the experiments. Blanks of samples were run in parallel to check that the sludge and soil samples did not contribute to the concentration of target compounds measured in the supernatants. Furthermore, control tests were run in the same tubes under the conditions as in sorption tests, using two concentration levels of all compounds (5 and 50 ng mL^{-1} for PFOS, PFOA and PFBS) and results showed that there were no any significant compound losses due to PFC sorption on the material used or degradation.

4.2.5. Quantification of sorption and desorption parameters

The sorption solid-liquid distribution coefficient, K_d (mL g^{-1}) was calculated as the ratio between the concentration of the target compound (PFOS, PFOA or PFBS) sorbed in the sludge or soil, C_s (ng g^{-1}), and its concentration in the aqueous phase at the equilibrium, C_{eq} (ng mL^{-1}) according to Eq. 3.1 (Section 3.2.7).

C_{eq} values were directly determined by LC-MS/MS and corresponding concentrations of PFCs sorbed in the sludge or soil, C_s were calculated by Eq. 3.2, taking into account the initial concentration of PFC added to the sludge or soil suspension, C_{in} (ng mL^{-1}) the volume of aqueous phase, V (mL) and the dry mass of sludge or soil sample m_S (g).

Moreover, the percentage of sorbed PFC, S (%), was calculated according to the following equation:

$$S\,(\%) = \frac{C_s \cdot m_s}{C_{in} \cdot V} \cdot 100 \qquad (4.1)$$

Similar to K_d (Eq. 3.1), the desorption solid-liquid distribution coefficient, $K_{d,des}$ (mL g^{-1}), was calculated as presented by Eq. 3.3, from $C_{s,des}$ (ng g^{-1}) and $C_{eq,des}$ (ng mL^{-1}), which are respectively the PFC concentration in the solid and in the liquid phase after the desorption experiment. $C_{eq,des}$ values were directly determined by LC-MS/MS, whereas $C_{s,des}$ was calculated as the difference between the initial concentration of PFC in the sludge or soil residue resulting from the sorption experiment, $C_{in,des}$ (ng g^{-1}), and the PFC desorbed referred to the mass of sludge or soil, as described by Eq. 3.4. As it was earlier explained, $C_{in,des}$ is C_s, corrected, when required, by the amount of PFC present in the residual volume of solution ($C_{eq} \cdot V_{res}$) that remained in the sludge or soil residue after the sorption experiment and can be easily calculated (Eq. 3.5).

Finally, the desorption yield, D (%), was calculated from the ratio between the amount of PFC desorbed and the amount of PFC present in the sludge or soil, previously to desorption experiment (Eq. 3.6).

4.2.6. Fitting of sorption and desorption isotherms

Sorption and desorption isotherms were constructed by plotting C_s *vs.* C_{eq}, K_d *vs.* C_s and $C_{s,des}$ *vs.* $C_{eq,des}$, $K_{d,des}$ *vs.* $C_{s,des}$. Isotherms were fitted to Freundlich and linear models and the same procedure described in section 3.2.8, for calculating fitting parameters (Eqs. 3.7 and 3.8) was used here.

4.3. Results and discussion

4.3.1. Sorption behaviour of PFCs in sewage sludge

4.3.1.1. Sorption isotherms of PFOS, PFOA and PFBS

The sorption isotherms of PFOS, PFOA and PFBS in the SL1 sludge sample are shown in Figure 4.2. Similarly shaped isotherms were obtained for the rest of sludge samples, as shown in Figures 4.3 - 4.5. Sorption isotherms (C_s vs. C_{eq}) of all three compounds followed a linear pattern for the concentration ranges studied, which was also demonstrated by the K_d *vs.* C_s isotherms, which showed near-to-zero slopes. Many organic substances follow this type of isotherms (Hinz, 2001; Higgins and Luthy, 2006), especially in porous materials, as sludges, which would allow PFC sorption in inner sorption sites (Ochoa-Herrera and Sierra-Alvarez, 2008).

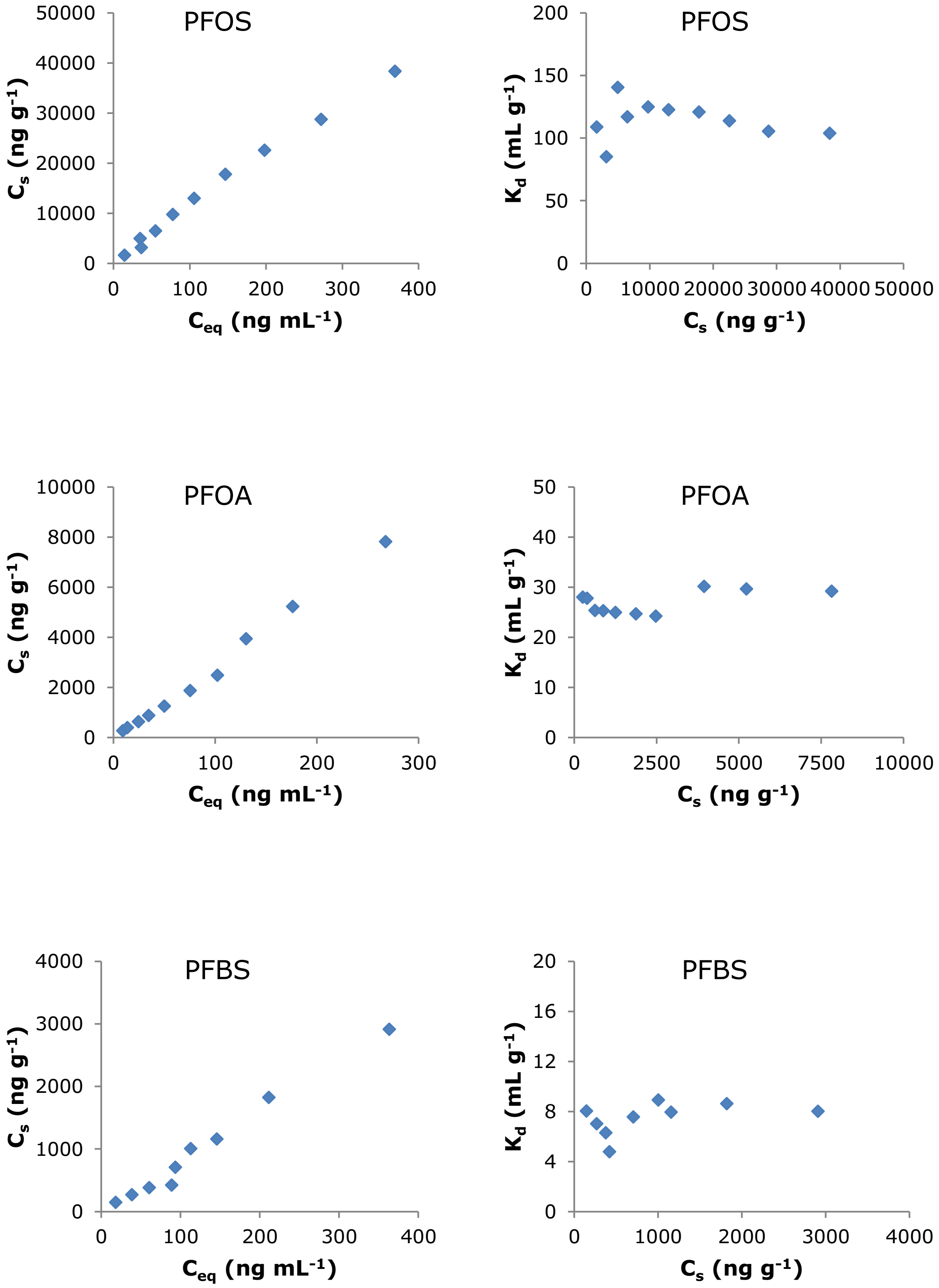


Figure 4.2. Sorption isotherms of PFOS, PFOA and PFBS in the SL1 sludge: C_s *vs* C_{eq} and K_d *vs.* C_s plots

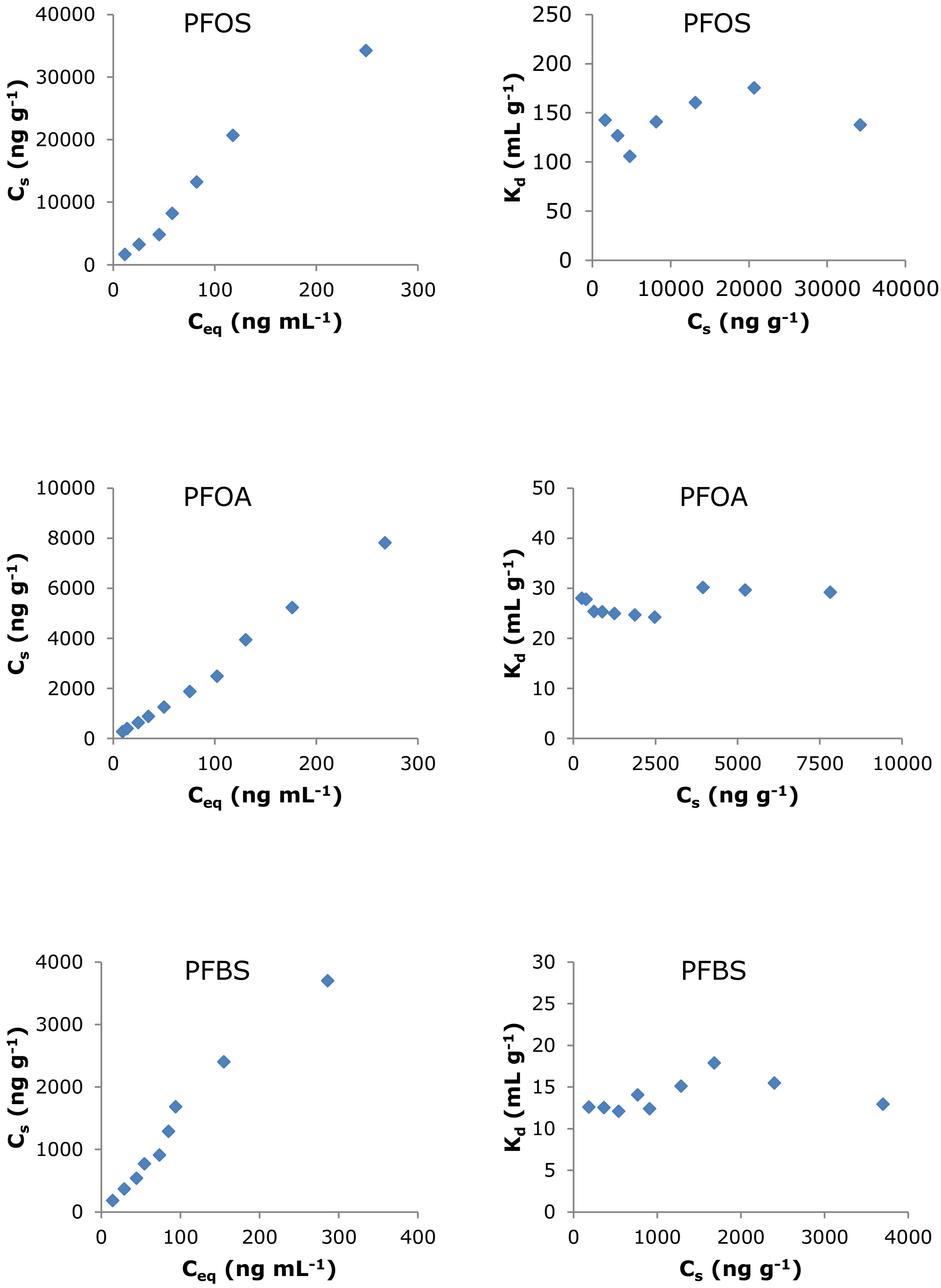


Figure 4.3. Sorption isotherms of PFOS, PFOA and PFBS in the SL3 sludge: C_s *vs.* C_{eq} and K_d *vs.* C_s plots

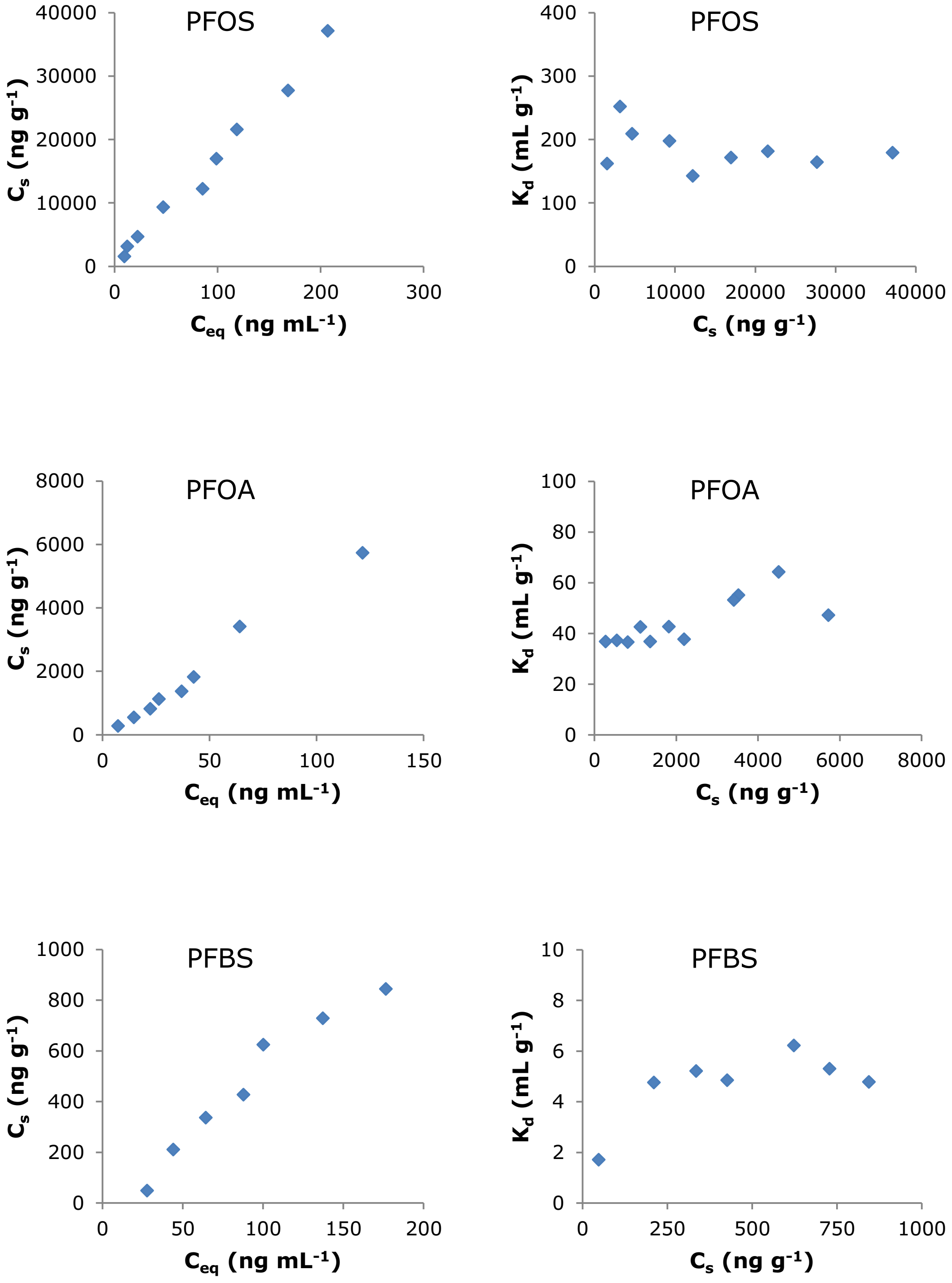


Figure 4.4. Sorption isotherms of PFOS, PFOA and PFBS in the SL4 sludge: C_s *vs.* C_{eq} and K_d *vs.* C_s plots

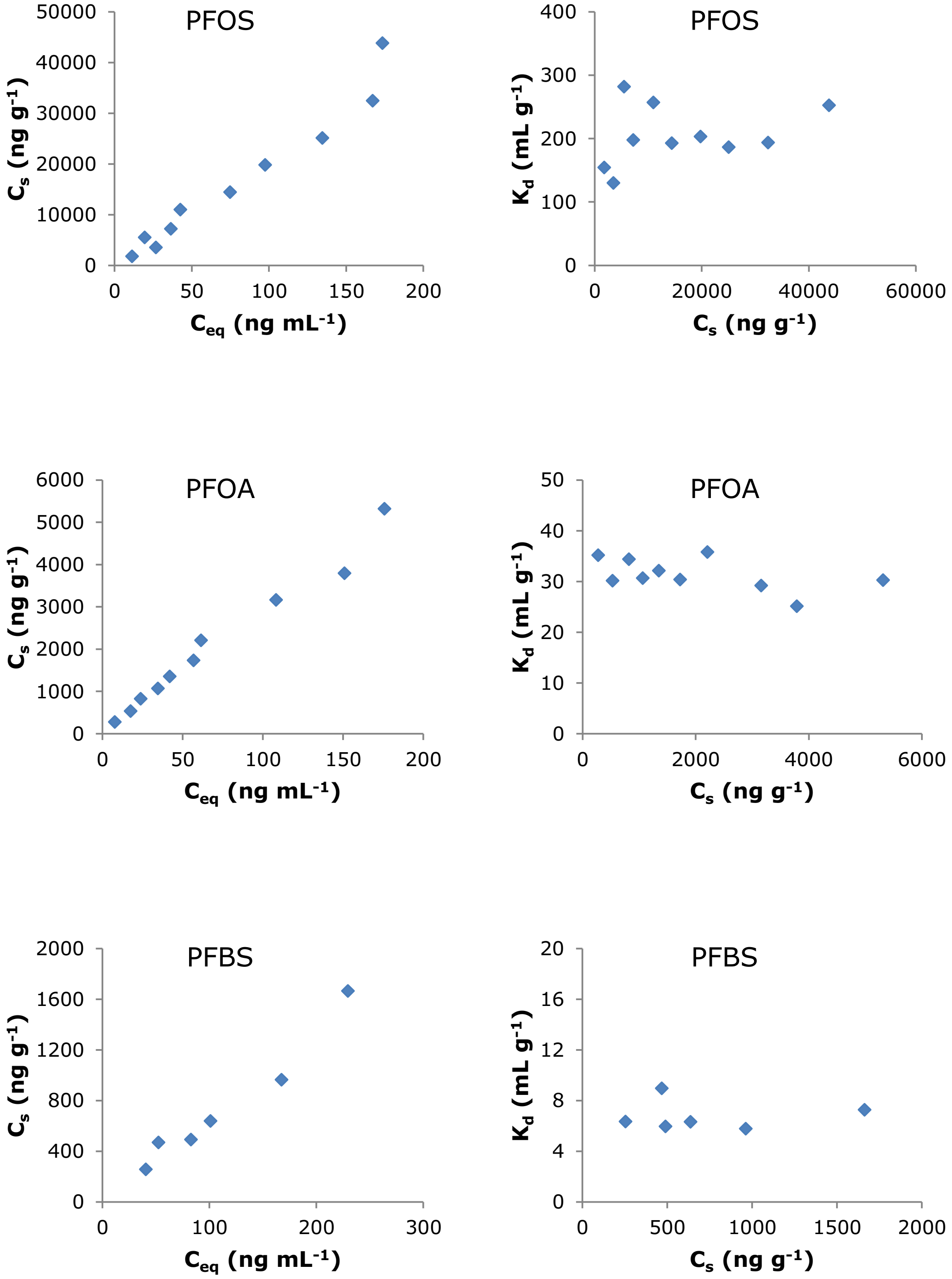


Figure 4.5. Sorption isotherms of PFOS, PFOA and PFBS in the SL5 sludge: C_s *vs.* C_{eq} and K_d *vs.* C_s plots

In agreement with linear-shaped isotherms, the experimentally obtained $K_{d,min}$ and $K_{d,max}$ values were similar: $K_{d,max}$ were often lower than two-fold $K_{d,min}$ values (see Table 4.4). The narrow interval of results in the sludge samples obtained for each compound, suggested that effect of sludge samples on the sorption of PFCs was much lower than the effect of the PFC, partially due to their similar OM content. On the other hand, K_d differences were higher regarding PFCs. If $K_{d,max}$ values were compared, a clear sequence of decreasing sorption was noticed from PFOS (140-281 mL g^{-1}), to PFOA (30-54 mL g^{-1}), with the lowest values for PFBS (7-18 mL g^{-1}).

Table 4.4. Sorption parameters obtained from the Freundlich and linear models for sorption isotherms of PFCs in analysed sludges

		Experimental data		**Freundlich fitting**		**Linear fitting**
PFC	**Sludge**	**$K_{d,min}$ (mL g^{-1})**	**$K_{d,max}$ (mL g^{-1})**	**N (SD)**	**K_F $ng^{(1-N)}$ mL^N g^{-1}**	**$K_{d,linear}$ (SD) (mL g^{-1})**
PFOS	**SL1**	85	140	1.0 (0.1)	129	104 (3)
	SL3	106	175	1.1 (0.1)	116	143 (10)
	SL4	143	252	1.0 (0.1)	161	171 (7)
	SL5	130	281	1.0 (0.1)	213	218 (17)
PFOA	**SL1**	24	30	1.0 (0.1)	25	30 (1)
	SL3	37	54	0.9 (0.1)	60	37 (1)
	SL4	36	53	1.1 (0.1)	32	50 (2)
	SL5	25	36	1.0 (0.1)	40	28 (1)
PFBS	**SL1**	5	9	1.0 (0.1)	6	8 (1)
	SL3	12	18	1.1 (0.1)	10	13 (1)
	SL4	2	7	1.0 (0.1)	5	5 (1)
	SL5	6	9	0.9 (0.1)	10	7 (1)

Despite the $K_{d,min}$-$K_{d,max}$ narrow ranges, fitting of the sorption isotherms to simple sorption equations permits to suggest the best-estimate values of the K_d for the PFC-sludge combinations examined here. Linearity of sorption isotherms was quantitatively confirmed by the fitting parameter N of the Freundlich model, which approached to 1 (Table 4.4). Moreover, the K_d values derived from the slope of the C_s *vs.* C_{eq} linear equation ($K_{d,linear}$) for the three PFCs correlated well with the K_F parameter values ($K_F = 0.94\ (0.06) \cdot K_{d,linear}$; $R^2 = 0.96$).

Experimental data for PFOS were in a good agreement with previously reported results, in which the K_d range for PFOS was 30-280 mL g^{-1} (Ochoa-Herrera and Sierra-Alvarez, 2008; Zhang et al., 2013). However, obtained values were much lower than those found by Zhou et al. (2010) (200-4050 mL g^{-1}), which can be attributed to the different nature of sludges and experimental conditions applied in deriving the K_d values. At the sludge pH, PFOS (and the rest of PFCs) are deprotonated and thus the anionic form predominates. This would lead to electrostatic repulsion to the negatively-charged sludge surface, although ion bridges with divalent cations existing in the sludge are also possible (Arvaniti et al., 2012). Considering that PFOS is the most hydrophobic of the PFCs investigated here, sorption mechanisms would be based either on hydrophobic interaction with functional groups of the sludge organic matter, or electrostatic interaction with the sludge surface through Ca+Mg ion bridge bonds (Zhou et al., 2010). The potential role of pH on PFOS sorption was minor in the examined sludges, as within their pH range (between 6 and 8) no significant effect could be expected on PFOS sorption due to changes in pH (Zhou et al., 2010). Thus, the highest sorption of PFOS among the PFCs investigated can be explained by a strong affinity of its long hydrophobic C-F chain to the sludge organic matter, predominantly involving Van der Waals interaction between perfluorinated chain of the PFOS and sludge organic matter. This was confirmed by the positive correlation obtained between $K_{d,linear}$ or K_F and the sludge organic matter content (for instance, $K_F = 5\ (1) \cdot OM$). The second mechanism was confirmed by the excellent correlations between Ca+Mg content in the sludge solution and the PFOS sorption parameters (for instance, $K_F = 68\ (4) + 1.04\ (0.04) \cdot (Ca+Mg)$; $R^2 = 0.99$).

The PFOA showed a lower sorption affinity for the sludge than PFOS, with consistently lower K_F and $K_{d,linear}$ values than those of PFOS. These results agreed with previous results (Zhang et al., 2013), in which K_d values for PFOA ranged from 13-68 mL g^{-1}, whereas one order of magnitude higher K_d values were obtained by Zhou et al. (2010), as already discussed for PFOS. However, our results agreed with the finding that PFOA had a lower sorption affinity to sludge than PFOS. The lower sorption of PFOA can be explained by the less hydrophobic character of PFOA, as deduced by its lower log K_{OW} due to the change in the hydrophilic group and the lower number of C-F bonds. Although the sludge organic matter alone did not govern PFOA sorption as much as for PFOS, Ca+Mg and OM multiple regression described well the PFOA sorption among the sludge samples investigated (for instance, $K_{d,linear} = 3.0\ (0.9) \cdot OM - 0.6\ (0.2) \cdot (Ca+Mg)$; $R^2 = 0.92$).

Sorption affinity of PFBS was the lowest among the PFCs examined. Similarly, low values for K_d (10-50 mL g^{-1}) were reported for PFBS sorption on sludge, although reported data are very restricted (Zhang et al., 2013). Comparing to PFOS and PFOA, the lowest sorption affinity of PFBS can be explained by its lowest hydrophobicity, as evidenced by the low value of its log K_{OW}, and explained by its shorter carbon chain. The relative low and constant values of K_F and $K_{d,linear}$ prevented to observe any significant correlation with sludge properties.

To confirm that hydrophobicity of the PFCs governed their sorption, $K_{d,linear}$ vs. log K_{OW} correlations were examined for the three compounds at each sludge sample. All correlations obtained had regression coefficients over 0.99, thus confirming the mechanisms controlling PFCs sorption in sludges.

4.3.1.2. Desorption isotherms of PFOS, PFOA and PFBS

Figure 4.6 shows, as an example, sorption and desorption isotherms of PFOS, PFOA and PFBS in the SL3 sludge, whereas the rest of desorption isotherms are shown in Figures 4.7-4.10.

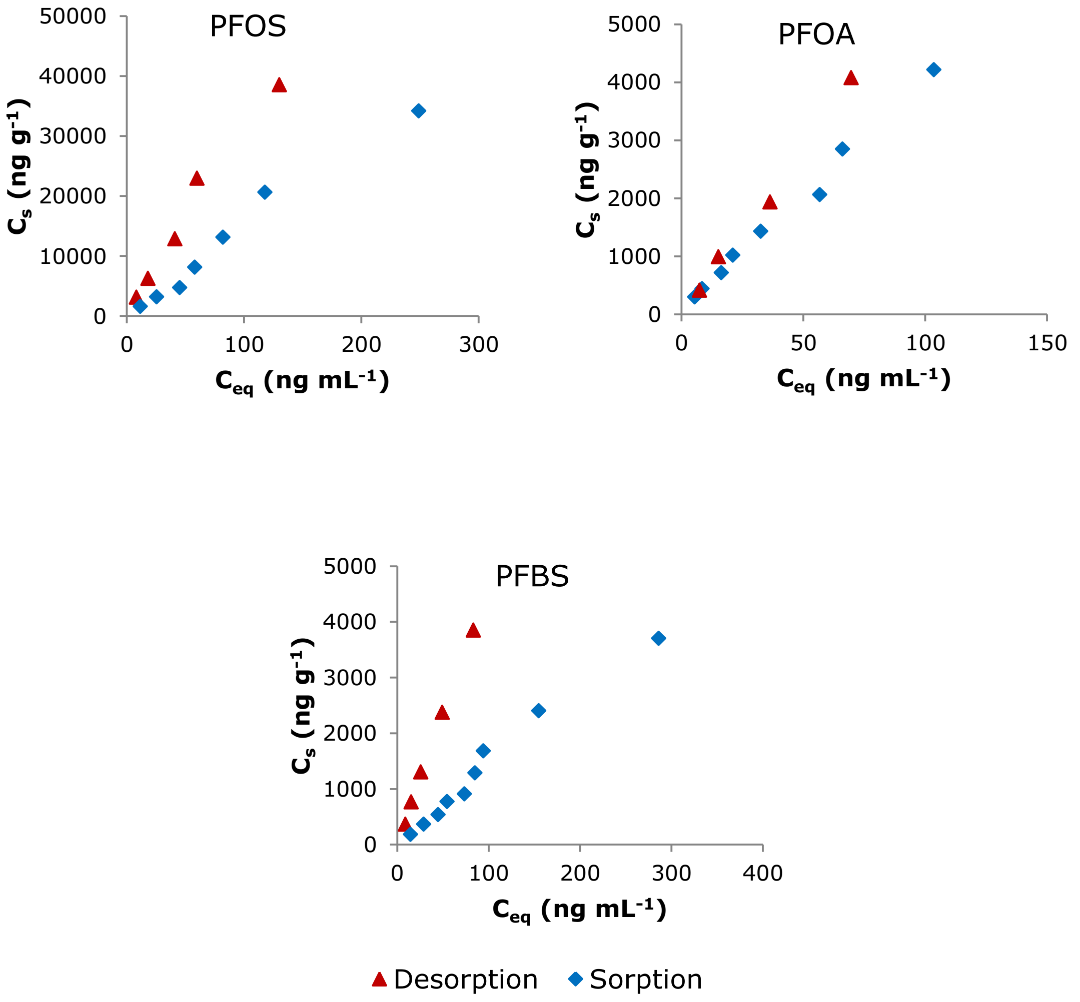


Figure 4.6. Sorption and desorption isotherms of PFOS, PFOA and PFBS in the SL3 sludge: C_s *vs.* C_{eq} plots

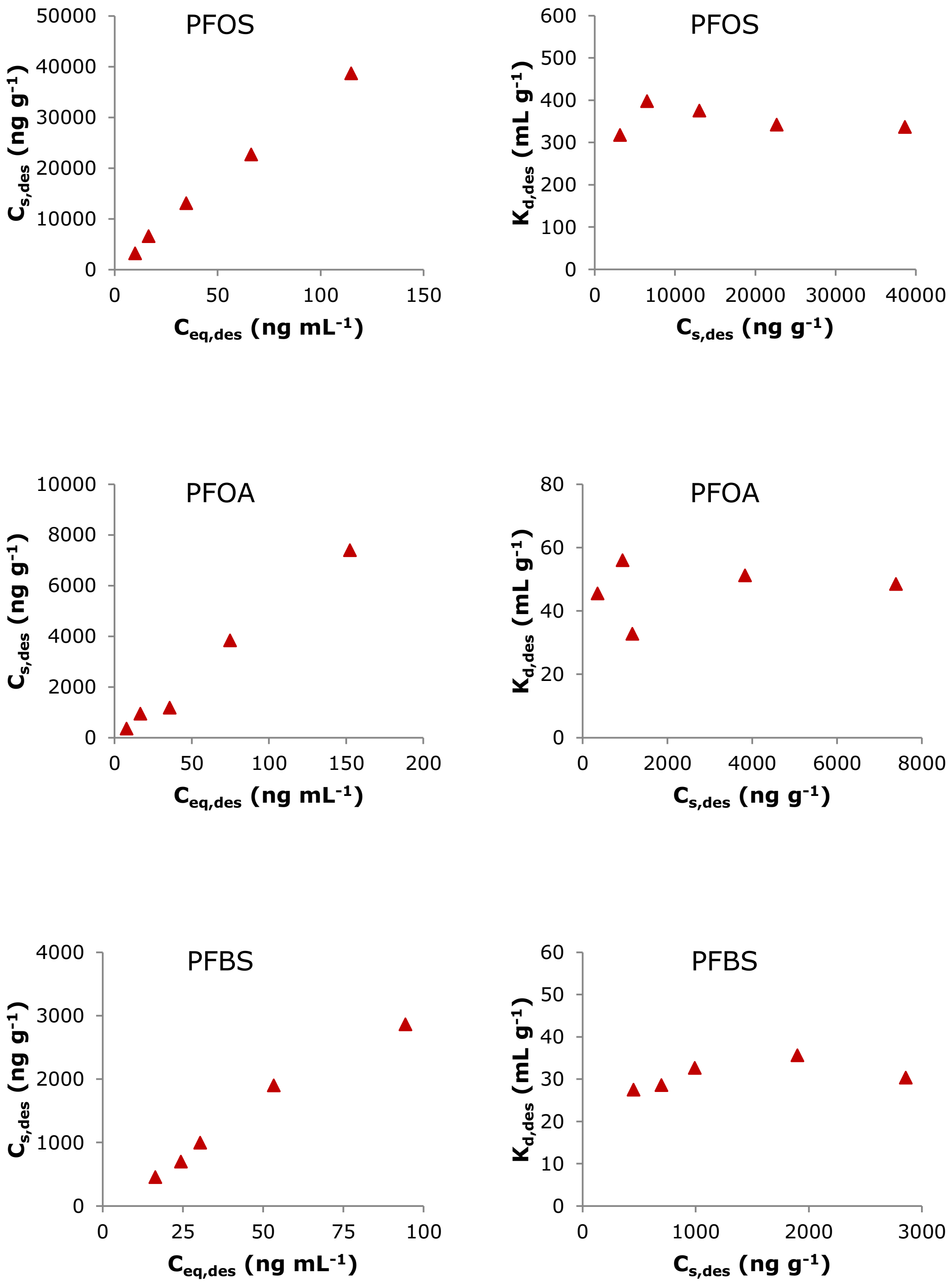


Figure 4.7. Desorption isotherms of PFOS, PFOA and PFBS in the SL1 sludge: $C_{s,des}$ *vs.* $C_{eq,des}$ and $K_{d,des}$ *vs.* $C_{s,des}$ plots

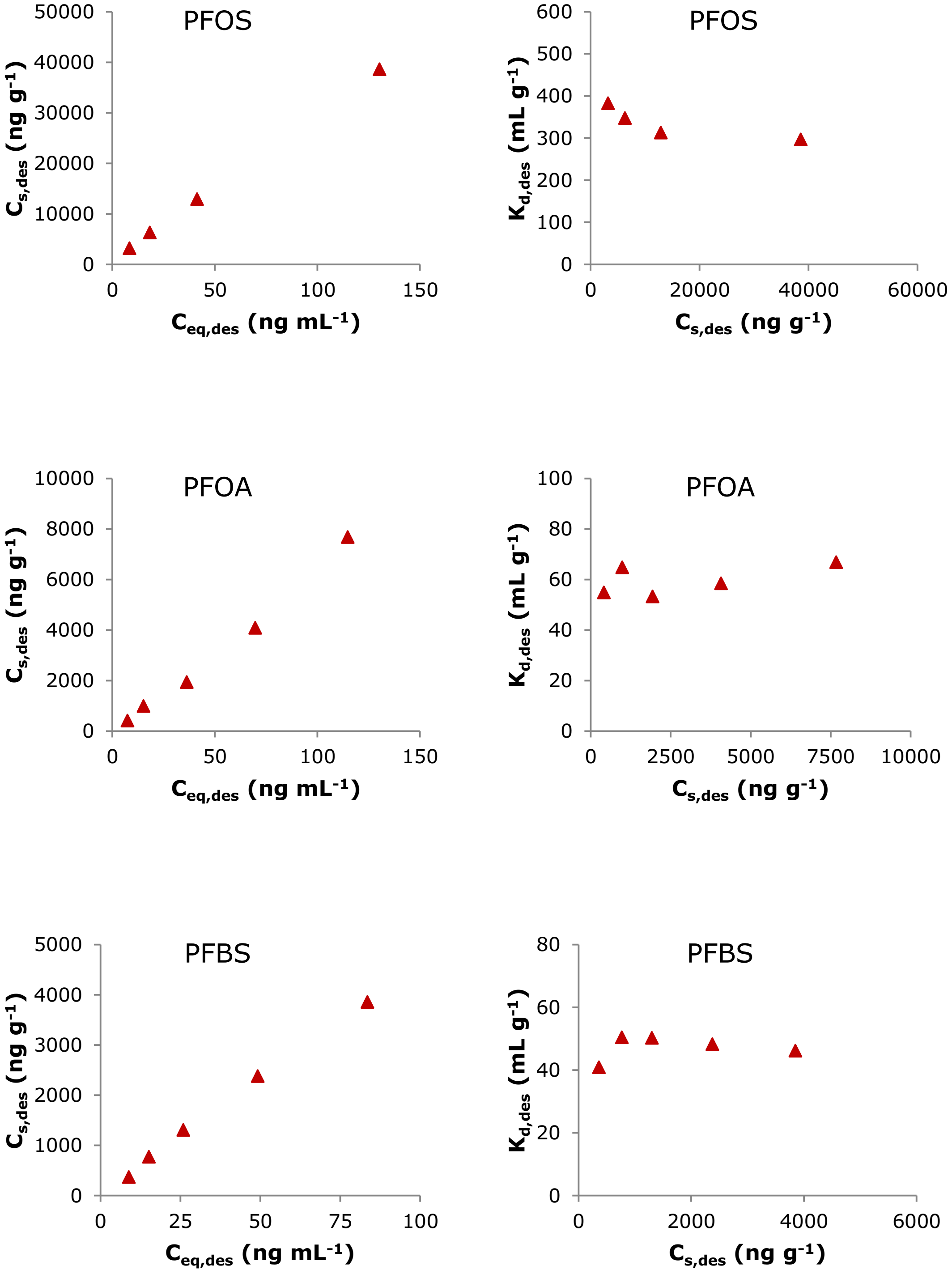


Figure 4.8. Desorption isotherms of PFOS, PFOA and PFBS in the SL3 sludge: $C_{s,des}$ *vs.* $C_{eq,des}$ and $K_{d,des}$ *vs.* $C_{s,des}$ plots

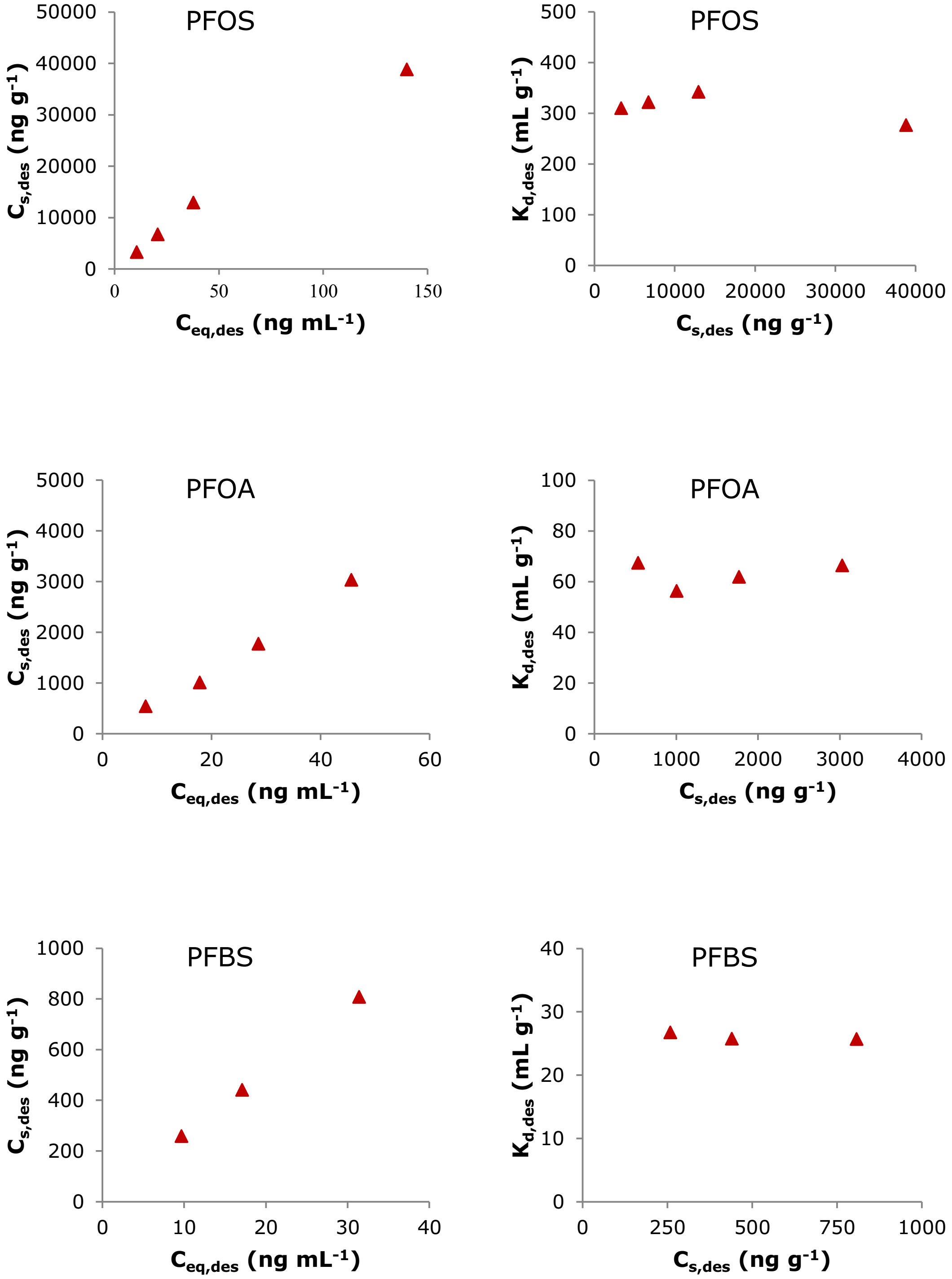


Figure 4.9. Desorption isotherms of PFOS, PFOA and PFBS in the SL4 sludge: $C_{s,des}$ *vs.* $C_{eq,des}$ and $K_{d,des}$ *vs.* $C_{s,des}$ plots

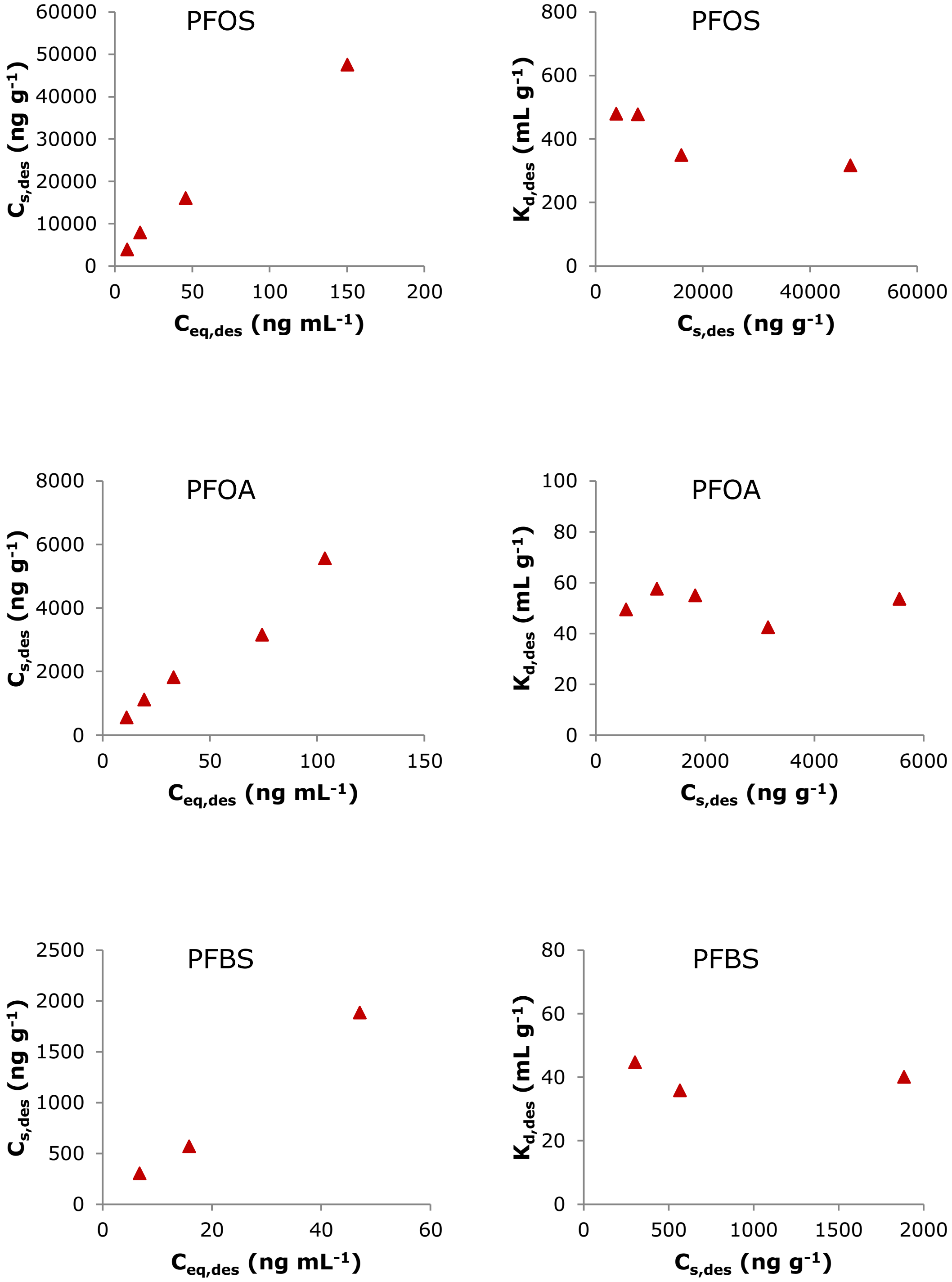


Figure 4.10. Desorption isotherms of PFOS, PFOA and PFBS in the SL5 sludge: $C_{s,des}$ *vs.* $C_{eq,des}$ and $K_{d,des}$ *vs.* $C_{s,des}$ plots

Desorption isotherms followed a linear pattern for the three compounds, as already seen in the sorption stage. Experimentally obtained desorption distribution coefficients, $K_{d,des,min}$ and $K_{d,des,max}$, varied within narrow ranges for every PFC (see Table 4.5), whereas the sequence of values observed also agreed with the previous sorption stage, as $K_{d,des}$ values decreased in the order PFOS > PFOA > PFBS, although values of the $K_{d,des}$ for PFOA and PFBS approached more than those of the previous sorption stage.

Desorption isotherm linearity was confirmed by the N_{des} parameter values, which did not differ from 1. Experimental data fitted well to Freundlich and linear equations, with regression coefficients higher than 0.97 for all sludge-compound combinations. Similar to sorption results, here $K_{d,des}$ and $K_{F,des}$ of PFCs were also similar in all samples and correlated well ($K_{F,des} = 1.5\ (0.1) \cdot K_{d,des,linear}$; $R^2 = 0.93$), although $K_{F.des}$ for PFOS appeared to be systematically higher than respective $K_{d,des,linear}$ (Table 4.5).

Table 4.5. Desorption parameters obtained from the Freundlich and linear model for desorption isotherms of PFCs in analysed sludges

PFC	**SL**	**Experimental data**		**Freundlich model**			**Linear model**	
		$K_{d,des\ min}$ (mL g^{-1})	**$K_{d,des\ max}$ (mL g^{-1})**	**N_{des} (SD)**	**$K_{F,des}$ ng$^{(1-Ndes)}$ mL^{Ndes} g^{-1}**	**$\frac{K_{F,des}}{K_F}$**	**$K_{d,des,linear}$ (SD) (mL g^{-1})**	**$\frac{K_{d,des,linear}}{K_{d,linear}}$**
PFOS	SL1	318	397	1.0 (0.1)	37	2.9	332 (8)	3.2
	SL3	296	382	0.9 (0.1)	458	3.9	299 (1)	2.0
	SL4	309	342	0.9 (0.1)	421	2.6	335 (9)	2.0
	SL5	349	479	0.9 (0.1)	697	3.3	367 (31)	1.7
PFOA	SL1	33	56	1.0 (0.1)	48	1.9	49 (3)	1.6
	SL3	53	67	1.0 (0.1)	53	0.9	67 (4)	1.8
	SL4	56	67	1.0 (0.1)	65	2.4	62 (4)	1.2
	SL5	42	58	1.0 (0.2)	58	1.5	50 (5)	1.8
PFBS	SL1	27	36	1.1 (0.1)	23	3.8	31 (2)	3.9
	SL3	41	50	1.0 (0.1)	43	4.3	46 (1)	3.5
	SL4	26	27	1.0 (0.1)	29	5.8	25 (1)	5.0

Desorption parameters were generally higher than the respective sorption parameters, with K_F and K_d ratios up to near 6 (see Table 4.5). This indicated that the sorption of PFCs was partially irreversible. This was confirmed by the desorption yields, which were summarized in Figure 4.11.

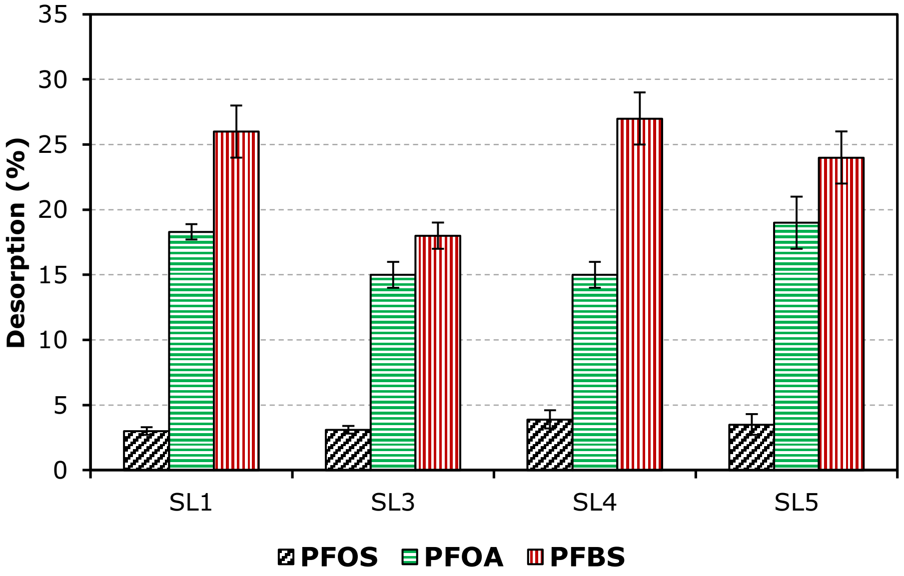


Figure 4.11. Desorption yield (%) of PFOS, PFOA and PFBS in the examined sludge samples

Desorption yields for PFOS were lower than 4% in all samples, thus confirming that this compound was irreversibly sorbed to the sludge, whereas desorption yields of PFOA and PFBS were much higher (15-19% and 18-27%, respectively). Therefore, PFOS showed both the highest sorption and the highest sorption irreversibility, which can also be attributed to its lowest water solubility and highest hydrophobicity among the PFCs examined. As for the sorption data, $K_{d,des}$ and log K_{OW} correlated well for the three PFCs at each sludge sample ($R^2 > 0.98$), thus confirming that PFC hydrophobicity was a key factor governing sorption and subsequent sorption reversibility of PFCs in sludges.

4.3.2. Sorption behaviour of PFCs in soils

4.3.2.1. Description of sorption isotherms of PFOS, PFOA and PFBS

The sorption isotherms of PFOS in the soils investigated are shown in Figure 4.12, whereas the sorption isotherms of PFOA and PFBS are shown in Figure 4.13. The sorption pattern of C_s *vs.* C_{eq} was considerably linear for all PFC-soil combinations at the concentration ranges studied, which was also confirmed by the nearly constant K_d values as a function of changes in C_s (Figures 4.14-4.16).

The almost constant partitioning of the three PFCs is also evidenced, in Table 4.6, by the similar values of $K_{d,min}$ and $K_{d,max}$ for a given PFC-soil combination, with a maximum difference of a factor two in many cases. In contrast, K_d differences were higher between PFCs. Among the studied PFCs, PFOS showed the highest K_d values, whereas for PFOA and PFBS, they were considerably lower. The sequence of K_d values for the three PFCs (PFOS > PFOA > PFBS) was in agreement with the respective physicochemical properties. Thus, PFOS with the lowest solubility and the highest hydrophobicity (Table 2.5) showed the highest K_d values (from 9-22 mL g^{-1} for ASCO to 243-444 mL g^{-1} for DUBLIN), whereas PFOA and PFBS, showed K_d values below 49 mL g^{-1} and 8 mL g^{-1}, respectively.

Within the results obtained for the same PFC, K_d values increased when increasing the organic matter of the soil, suggesting that the main sorption mechanism of PFCs, is based predominantly on Van der Waals interactions between the the non-polar and hydrophobic C-F chain of the compound and the soil organic matter, as suggested by Karickhoff (1981).

The sorption percentages of PFOS in soils were in a broad range (from 46 to 97%) and systematically increased in soils with a higher OC content of the soil (Table 4.5), in the same way as K_d values. In contrast, the sorption percentages of PFOA and PFBS were much lower, from 18 to 81% and from 6% to 40%, respectively, and were only significant for those soils with a higher organic matter content, such as OVI01 and DUBLIN.

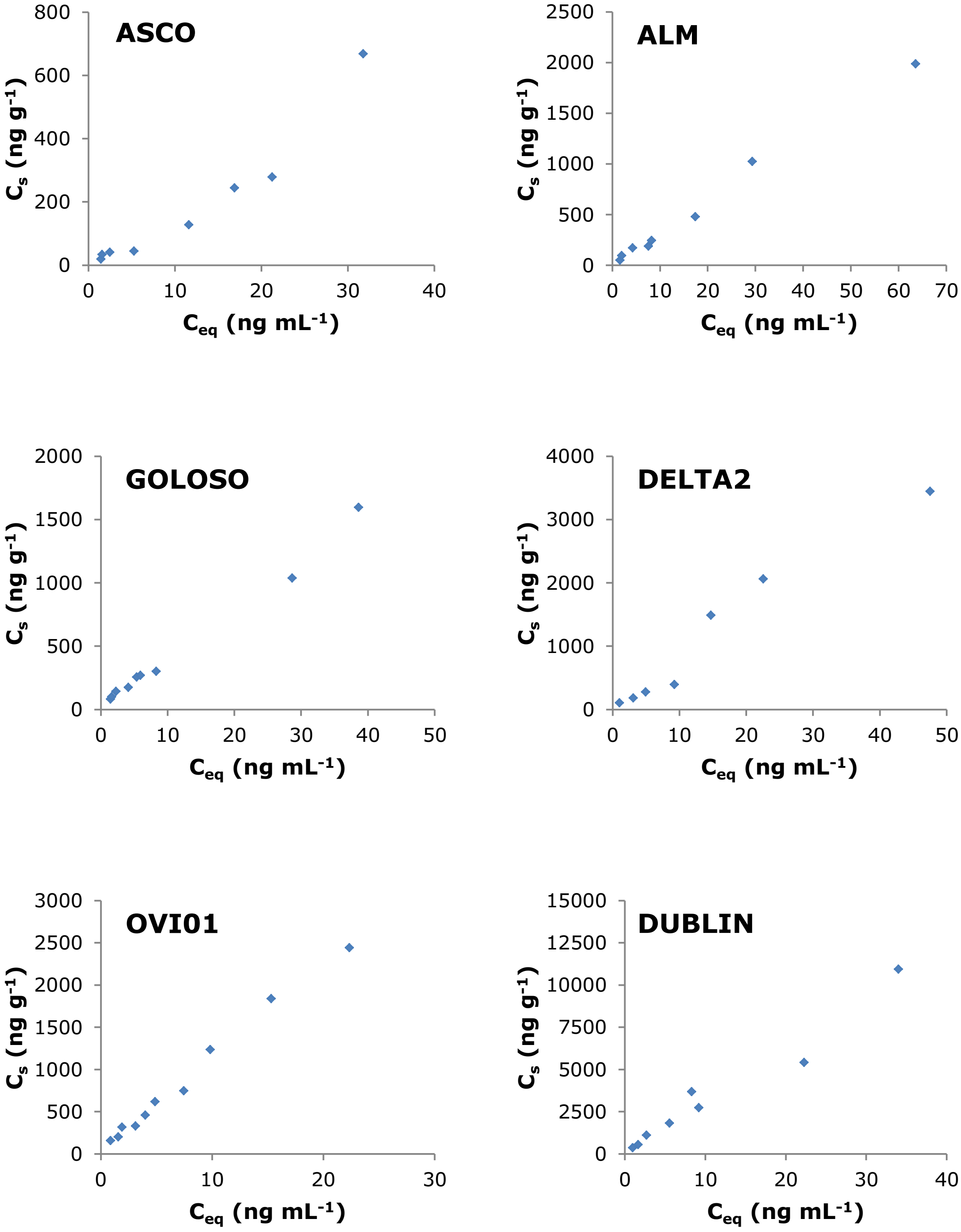


Figure 4.12. Sorption isotherms of PFOS in analysed soils: C_s *vs.* C_{eq} plots

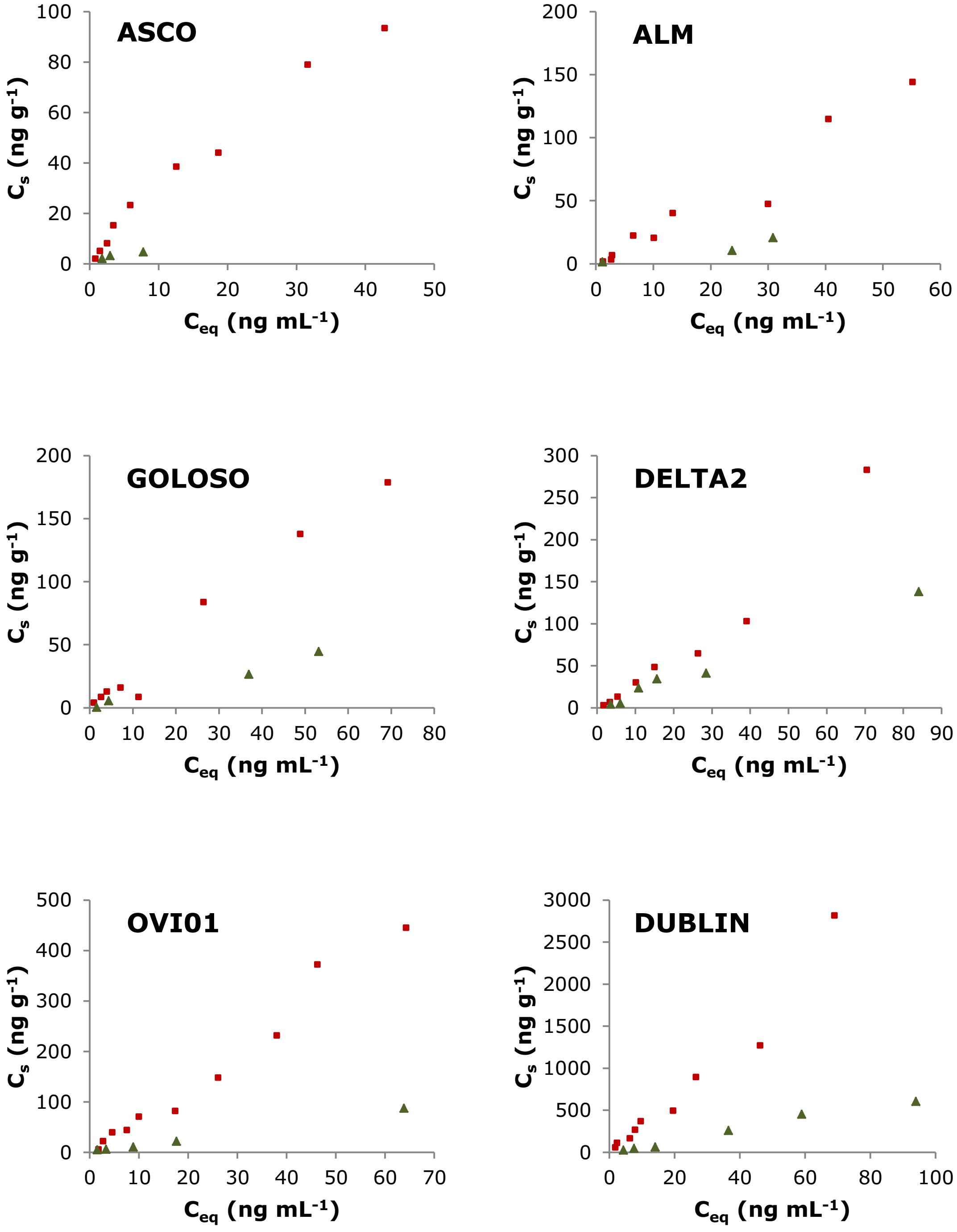


Figure 4.13. Sorption isotherms of PFOA (■) and PFBS (▲) in analysed soils: C_s *vs.* C_{eq} plots

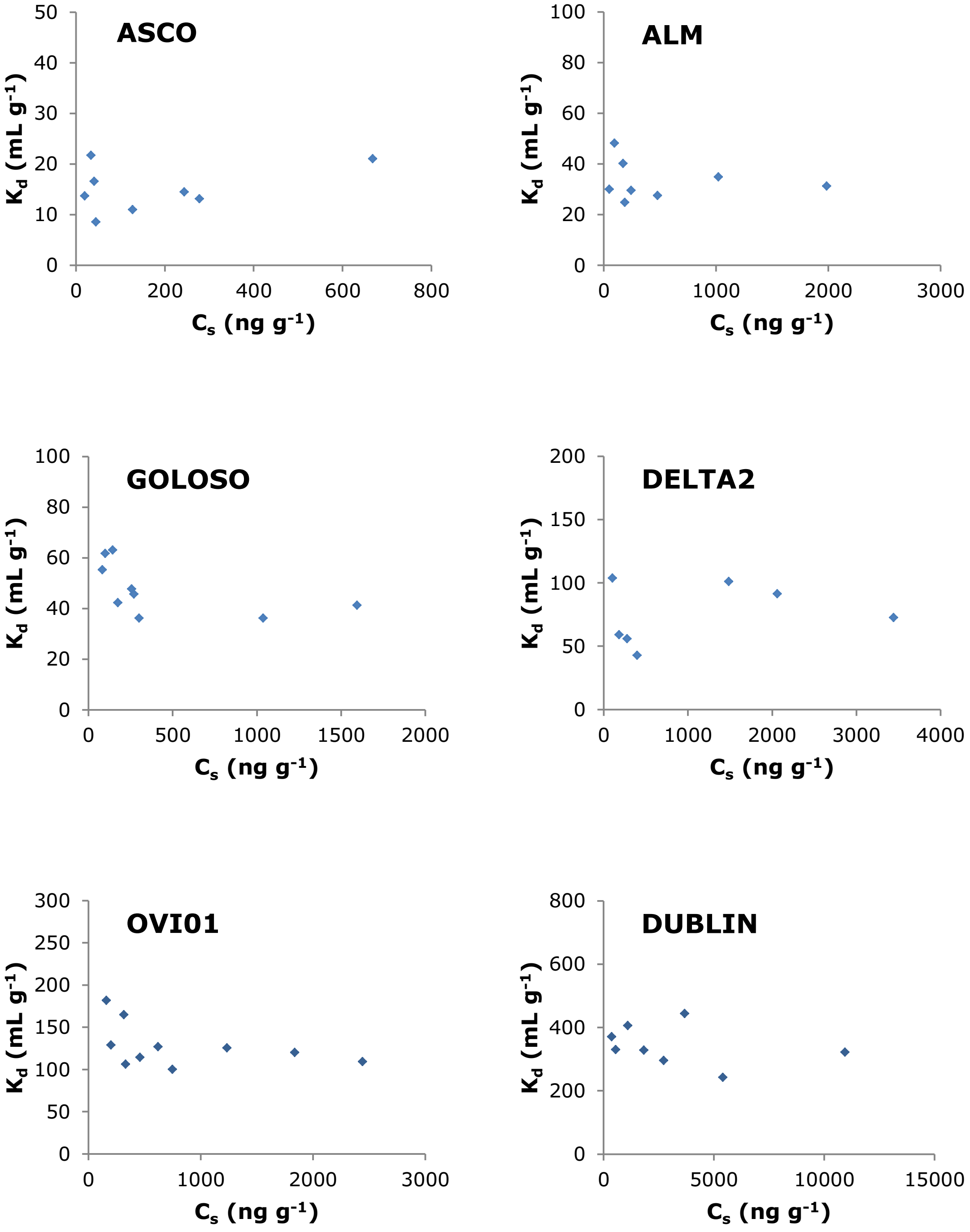


Figure 4.14. Sorption isotherms of PFOS in analysed soils: K_d *vs.* C_s plots

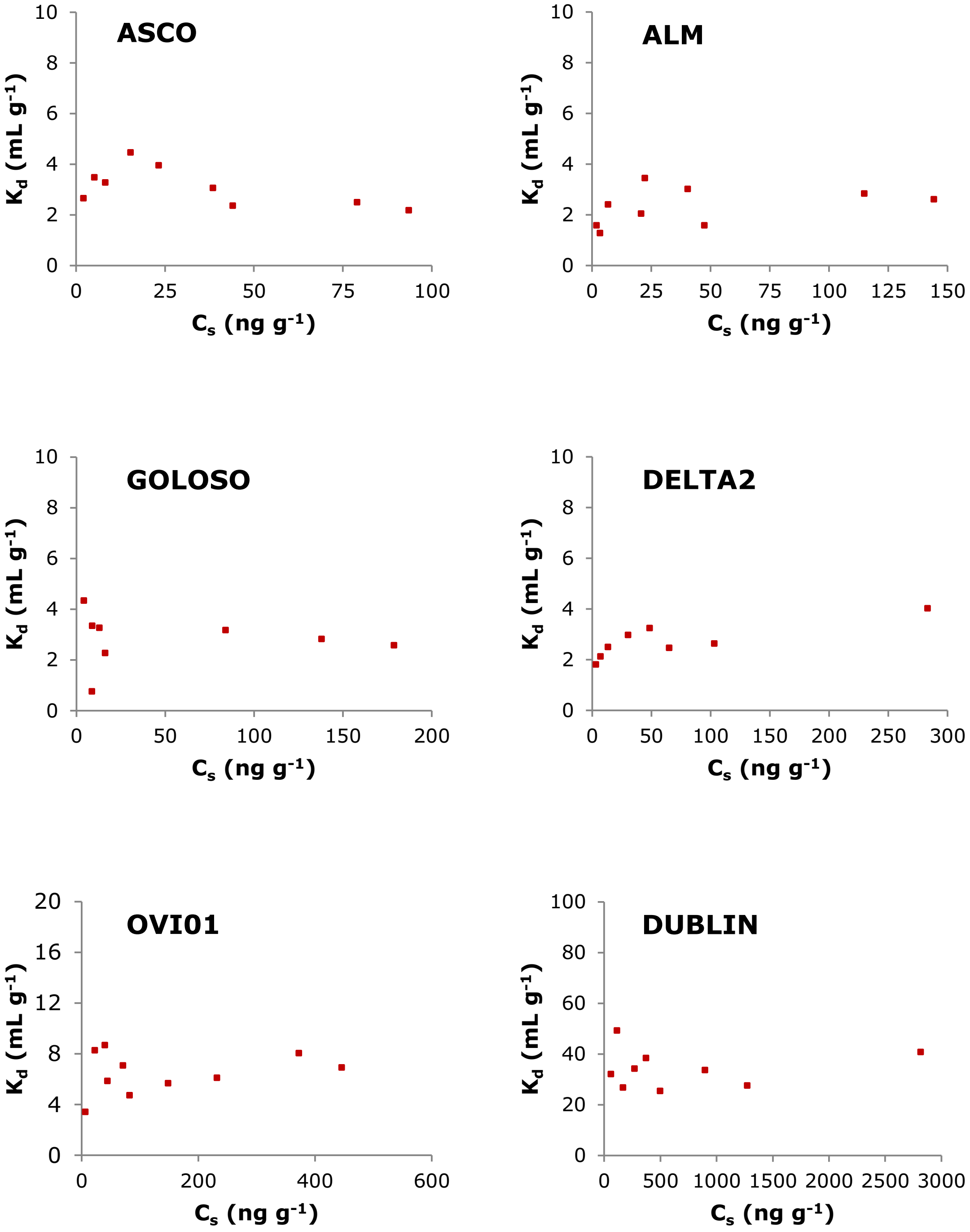


Figure 4.15. Sorption isotherms of PFOA in analysed soils: K_d *vs.* C_s plots

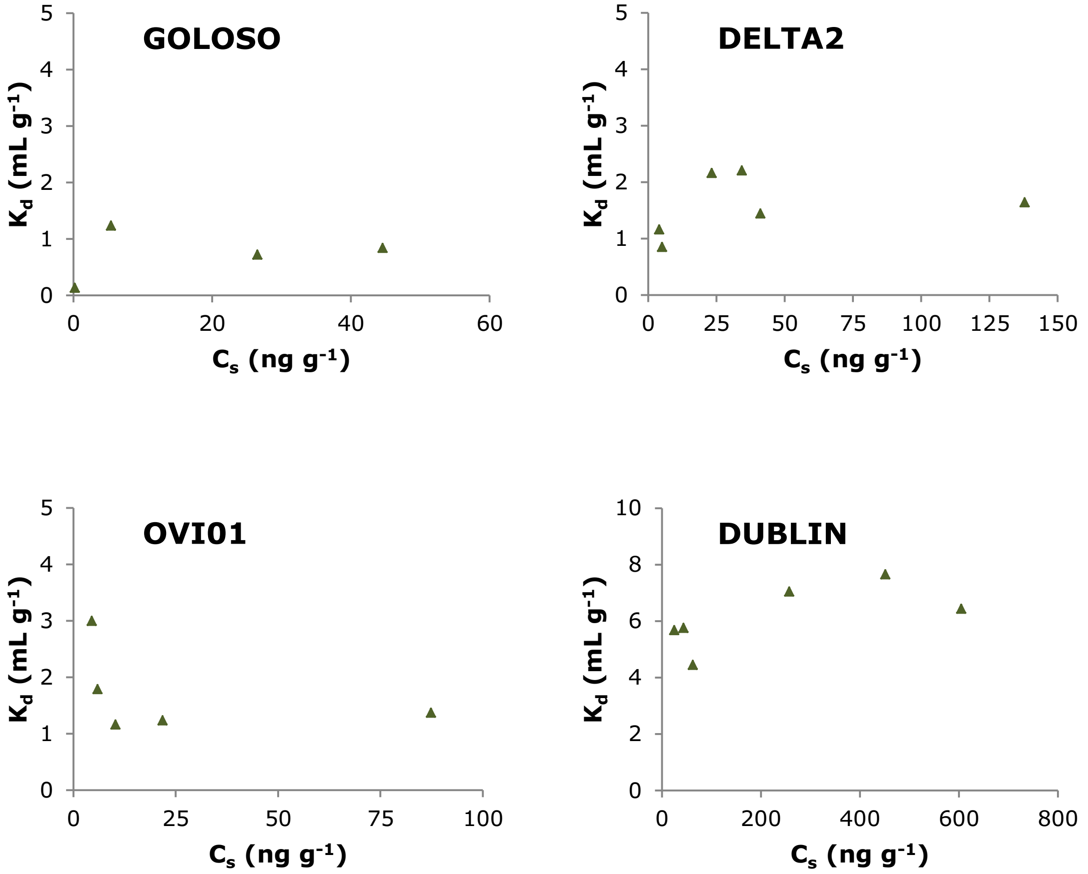


Figure 4.16. Sorption isotherms of PFBS in analysed soils: K_d *vs.* C_s plots

4.3.2.2. Fitting of sorption isotherms

In order to confirm the linearity of C_s *vs.* C_{eq} and to deduce a best-estimate K_d value for each PFC-soil combination, the sorption isotherms were fitted to the Freundlich and linear models, except for PFBS in ASCO and ALM soils, with an extremely low sorption, which made it difficult to obtain good fitting. In these two cases, the small number of data only permitted to derive a K_d value from the linear model. The values of the N and K_F parameters obtained from the Freundlich fitting, as well as the $K_{d,linear}$ values derived from the slope of the C_s *vs.* C_{eq} correlation are shown in Table 4.6. Values of N obtained from the Freundlich fitting were close to 1 for all PFC-soil combinations, confirming the constant partitioning of PFCs in all soils. Moreover, the $K_{d,linear}$ and K_F values for the three PFCs in soils were well correlated (K_F = 1.3 (0.1) · $K_{d,linear}$; R^2 = 0.99). According to Karickhoff (1981), sorption linearity can be partially explained by the fact that C_{eq} values of PFCs, at the environmental levels considered in the present work, were below one half of their solubility in water (values shown in Table 2.5). Linearity of sorption isotherms also agreed with previously reported results for PFCs (Enevoldsen and Juhler, 2010; Chen et al., 2013).

The $K_{d,linear}$ data for PFOS obtained in this were in good agreement with previous works, which obtained K_d values in the range 12 - 17 mL g^{-1} for soil samples containing less than 1% of organic carbon (Chen et al., 2009; Enevoldsen and Juhler, 2010), similar to those obtained for ASCO sample (OC = 0.2%). Furthermore, Chen et al. (2013) also reported very similar K_d values, from 7.3 to 115 mL g^{-1}, in five soils with OC ranging from 0.5 to 16%.

Regarding PFOA, the $K_{d,linear}$ values were very low, in comparison with PFOS, for the concentration range studied, varying from 2.2 to 38 mL g^{-1}. These results also are in agreement with K_d values reported by Chen et al. (2013), ranging from 2.3 to 16.1 mL g^{-1} for soils with OC from 0.5 to 16%. Finally, $K_{d,linear}$ values obtained for PFBS were extremely low, from 0.4 mL g^{-1} for ASCO to 7 mL g^{-1} for DUBLIN (Table 4.6). The $K_{d,linear}$ obtained for ASCO agreed with the K_d value of 0.41 mL g^{-1} reported by Enevoldsen and Juhler (2010) for PFBS in a soil with 1% of OC.

Table 4.6. Sorption parameters obtained from the Freundlich and linear model for PFOS, PFOA and PFBS sorption in the analysed soils

PFC	**Soil**	**Experimental data**				**Freundlich**		**Linear**
		$K_{d,min}$	**$K_{d,max}$**	**S_{min}**	**S_{max}**	**N (SD)**	**K_F**	**$K_{d,linear}$ (SD)**
PFOS	ASCO	9	22	46	68	1.0 (0.1)	17	19 (2)
	ALM	25	48	71	83	0.9 (0.1)	41	32 (1)
	GOLOSO	35	63	78	86	0.9 (0.1)	61	38 (2)
	DELTA2	43	104	81	91	1.0 (0.1)	86	76 (7)
	OVI01	100	182	91	95	0.9 (0.1)	157	110 (4)
	DUBLIN	243	444	95	97	0.9 (0.1)	389	295 (25)
PFOA	ASCO	2.4	4.0	18	31	0.9 (0.1)	4	2.2 (0.1)
	ALM	1.3	3.5	11	26	1.1 (0.2)	2	2.6 (0.2)
	GOLOSO	0.8	4.3	7	30	0.9 (0.1)	4	2.7 (0.2)
	DELTA2	1.8	4.0	15	29	1.1 (0.1)	2	3.9 (0.3)
	OVI01	3.4	8.7	25	46	1.0 (0.1)	7	7.1 (0.4)
	DUBLIN	25	49	70	81	1.0 (0.2)	40	38 (3)
PFBS	ASCO	0.6	1.2	6	10	-	-	0.4 (0.1)
	ALM	0.4	1.2	4	11	-	-	0.6 (0.2)
	GOLOSO	0.1	1.2	1	11	0.9 (0.2)	1.3	0.8 (0.1)

4.3.2.3. Sorption reversibility of PFCs

Desorption yields from the desorption tests carried out in the five soil samples are shown in Figure 4.17. The lowest desorption yields were found for PFOS (D < 13%), thus indicating that the sorption of this compound in soils was highly irreversible. PFOA and PFBS behaved in a similar way, showing much higher desorption yields, from 24 to 58 and from 32 to 60%, respectively.

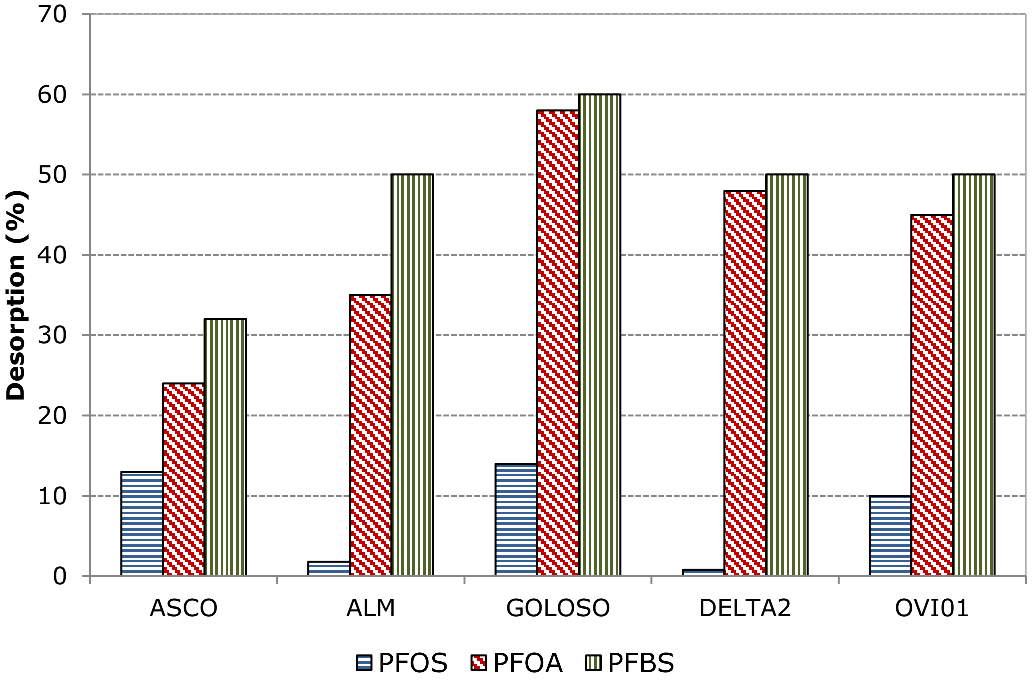


Figure 4.17. Desorption (%) of PFOS, PFOA and PFBS in five soils

Therefore, PFOS showed both the highest sorption and the lowest sorption reversibility, which can also be attributed to its lowest water solubility and highest hydrophobicity among the PFCs examined. Therefore, the important role of hydrophobic interaction in the sorption mechanism was confirmed.

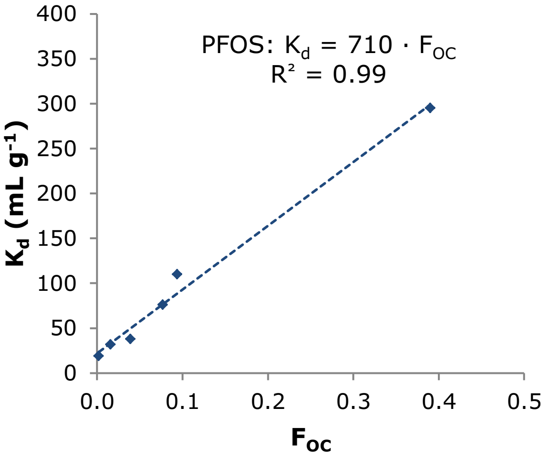
4.3.2.4. Correlation of K_d with soil characteristics

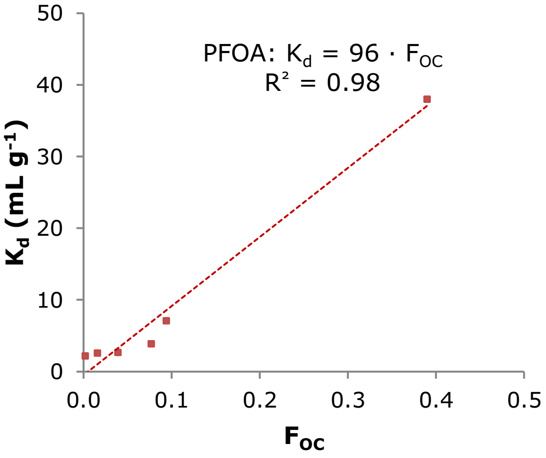
As the OC content played a major role in the variation of the sorption parameters of PFCs in the soils investigated, it was suggested to further explore the relationship between the K_d and the fraction of organic carbon in soil, F_{OC} (expressed as gram of OC per gram of soil). The K_d of organic compounds in soils can be expressed as the sum of two contributions, the $K_{d,MIN}$ which describes the sorption of the compound on the mineral fraction of soil, basically attributed to the hydrophilic part of the molecule; and the $K_{d,ORG}$ which would correspond to the hydrophobic interaction with the organic matter fraction:

$$K_d = K_{d,ORG} + K_{d,MIN} = K_{OC} \cdot F_{OC} + K_{d,MIN} \qquad (4.2)$$

where $K_{d,ORG}$ can be expressed as the product of the solid-liquid distribution coefficient of the compound in the organic fraction (referred to the weight of organic carbon), K_{OC}, and the fraction of organic carbon in the soil, F_{OC}. Therefore, a K_{OC} value for a given PFC can be derived from the slope of the K_d *vs.* F_{OC} correlation obtained in various soils.

Figure 4.18 plots the correlations obtained for the three PFCs investigated in this work. The strong dependence between the K_d values and the soil organic carbon for PFOS, PFOA and PFBS (R^2 = 0.99, 0.98 and 0.99, respectively) allowed to deduce K_{OC} values from the slope of the curves, showing that PFOS (K_{OC} = 710 (39) mL g^{-1}) presented a higher sorption in organic matter than PFOA (K_{OC} = 96 (7) mL g^{-1}) and PFBS (K_{OC} = 16.7 (0.7) mL g^{-1}). Although individual K_{OC} values could be obtained for each soil, a K_{OC} derived from the correlation would be more representative of a series of soils with a broad range of OC contents, as is the case of the present work, since soils with an extremely low OC content might overestimate K_{OC} value. The values for the intercepts ($K_{d,MIN}$) were not statistically different to zero, thus indicating the negligible role of the soil mineral fraction in the sorption pattern of three compounds. This was consistent with the proposed sorption mechanism.





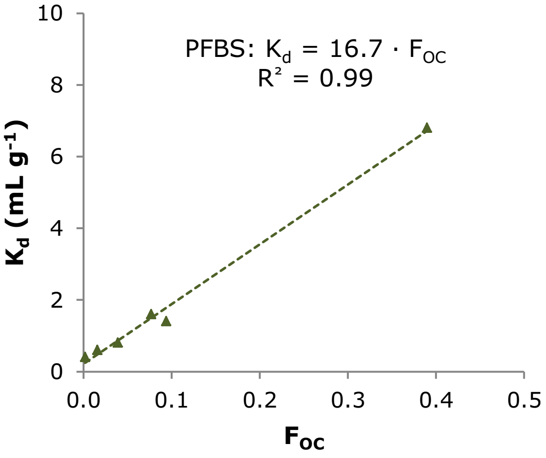


Figure 4.18. Relation of K_d for PFOS, PFOA and PFBS to the fraction of organic carbon in analysed soils

The deduced log K_{OC} values for PFOS (2.9) and PFOA (2.0) were similar to reported values of 2.8 - 3.2 for PFOS and 2.0 - 2.6 for PFOA, originated from similar experiments (Chen et al., 2013), but lower than the reported values of 3.1 - 3.6 for PFOS (Chen et al., 2009) and 2.2 - 2.6 for PFOA (Enevoldsen and Juhler, 2010), corresponding to soils with a very low OC content (< 1%). The log K_{OC} for PFBS (1.2) was similar to the reported values of 1.2 - 1.6 obtained by Enevoldsen and Juhler (2010).

A good correlation obtained between the log K_{OC} values and the log K_{OW} of studied compounds (log K_{OC} = 0.48 (0.04) · log K_{OW}; R^2 = 0.84) confirmed that not only the soil characteristics, but also the physicochemical properties of PFCs influenced their sorption pattern in soils with known organic carbon content.

K_d values for PFOS and PFBS were well correlated (K_d (PFOS) = 42 (4) · K_d (PFBS); R^2 = 0.97), which provided information about the influence of the length of perfluorinated carbon chain on the sorption of PFCs in soils. Based on the difference between the log K_{OC} values of PFOS and PFBS (1.6 log units) it can be suggested that each CF_2 moiety increased the log K_{OC} value for about 0.4 log units. This value cannot be compared with previous results, due to the lack of available information on the impact of CF_2 moiety in soils. Nevertheless a similar value, of 0.5 log units, was reported in similar environmental matrices, such as sediments (Higgins and Luthy, 2006). Therefore, this observation supported the suggestion that sorption of the anionic PFCs into the soil organic matter was the dominant mechanism of sorption.

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Chapter 5. Conclusions

With respect to the first main objective of the thesis, which deals with the leaching of APCs and heavy metals in sludges, the following conclusions can be drawn:

- Sewage sludge drying at 40 °C affected the characteristics of sludge organic matter, and thus the leaching pattern of pollutants. The drying treatment degraded organic compounds into simpler molecules, thus leading to changes in the total organic carbon, a decrease in the contribution of the relative particulate organic carbon in solution, and a concomitant increase in the dissolved organic carbon.

- The leaching yields of OP, NP and NP_1EO ranged from 1.3 to 35% for fresh sludge samples and from 0.8 to 3.4% for dried samples. Whereas sludge pH and organic carbon in the solid phase also affected APC leaching, the main mechanisms affecting the decrease in the leaching of APCs was attributed to their association with particulate organic matter, which had a significantly lower concentration in dried than in fresh sludge samples.

- Generally, leaching of heavy metals was very low (< 5%) in both fresh and dried sludge samples, with an exception of Cu and Ni, whose leaching in dried samples was up to 43 and 12%, respectively. However, these results did not indicate an environmental risk because the total content of heavy metals in sewage sludge is already regulated.

- Changes in the leaching pattern of APCs due to sludge drying cannot be easily extrapolated to other families of compounds. For instance, results evidenced that the leaching of heavy metals could increase. However, it was hypothesized that, in a similar way to APCs, leaching of other hydrophobic organic compounds could decrease. Thus, drying of sewage sludges is recommended before their potential addition to agricultural soils.

Regarding the second objective of this work, which relates to the sorption behavior of APCs in soils, it can be concluded that:

- Sorption solid-liquid distribution coefficients, K_d, varied within nearly two orders of magnitude ranges in the investigated soils (from 25 to 1060 mL g^{-1} for NP and from 51 to 740 mL g^{-1} for NP_1EO). K_d values were usually higher for NP than for NP_1EO, as NP hydrophobicity (log K_{OW} (NP) = 4.5) was higher than that of the mono-ethoxylate derivate (log K_{OW} (NP_1EO) = 4.2).

- A linear fitting model was generally appropriate to describe the sorption of NP and NP_1EO in soils. The sorption mechanisms were based on a hydrophobic interaction between the hydrophobic alkyl chain of APCs and the organic fraction of soils. Exception to this pattern was the sorption of NP_1EO in those soils with the highest DOC/OC ratio. These latter isotherms were better described by the Freundlich equation with $N > 1$, due to the competition between the organic matter in solution and that in the solid phase for NP_1EO sorption at low initial concentrations.

- As organic carbon content governed the sorption of NP and NP_1EO in soils, log K_{OC} values could be deduced for NP and NP_1EO, which were 4.0 and 3.8, respectively. These log K_{OC} values were lower than those of other organic pollutants, such as polycyclic aromatic hydrocarbons and polychlorinated biphenyls, indicating that soils have a lower sorption affinity for the APCs.

- NP and NP_1EO desorption isotherms also followed a linear pattern. Desorption solid-liquid distribution coefficients, $K_{d,des}$, varied in the range of 130-1470 mL g^{-1} for NP and 25-1285 mL g^{-1} for NP_1EO in the examined soils. Results pointed out that $K_{d,des}$ were higher than K_d values, thus indicating that the sorption of target compounds was highly irreversible. This is a positive finding from the standpoint of potential repeated additions of sewage sludge to agricultural soils, because the APCs potentially incorporated in soils will remain irreversibly sorbed and, thus, immobilized by the soil matrix.

With respect to the third objective of this doctoral thesis, which deals with the sorption behaviour of PFCs in sewage sludges and soils, the following main conclusions can be drawn:

- Both the Freundlich and linear isotherms provided good fit for the sorption behaviour of PFCs in sludges. K_d values for each PFC in the sludges examined, ranged in a narrow interval ($K_{d,linear}$: 105 - 220 mL g^{-1} for PFOS; 30 - 50 mL g^{-1} for PFOA; and 5 - 13 mL g^{-1} for PFBS), suggesting that the effect of sludge characteristics on the sorption of PFCs was much lower than the effect of the PFC, partially due to the similar organic matter content in sludges. In agreement with the log K_{OW} sequence, sorption affinity of the PFCs for the sludge decreased in the following order: PFOS > PFOA > PFBS.

- $K_{d,linear}$ (and K_F) for both PFOS and PFOA correlated well with the sludge organic matter content and with the Ca+Mg content in sludge solutions, thus confirming that the sorption occurred via the hydrophobic interaction between pefluorinated carbon chain and the organic matter of sludge, with a potential additional role of Ca/Mg ion bridges to overcome the electrostatic repulsions of deprotonated PFCs with the negatively charged surface sites of sludges at the sample pH. Low values of the sorption parameters for PFBS prevented any correlation to be established.

- Similarly to that observed in sludges, both the Freundlich ($N \approx 1$) and linear models appropriately described sorption of PFCs in soils. The dominant interaction of PFCs in soils was also suggested to be of hydrophobic character, predominantly Van der Waals forces between hydrophobic perfluorinated carbon chain and the organic matter in the soil solid phase.

- The $K_{d,linear}$ values of PFCs in the investigated soils were 19 - 295 mL g^{-1} for PFOS, 2.2 - 38 mL g^{-1} for PFOA, and 0.4 - 6.8 mL g^{-1} for PFBS, depending on the soil considered. Therefore, soil sorption affinity for PFCs decreased in the following order: PFOS > PFOA > PFBS, which confirmed that the PFC physicochemical properties, especially hydrophobicity, influenced their sorption behaviour in soils.

- The K_d values of PFCs correlated well with the fraction of soil organic carbon, which provided an estimation of the log K_{OC} values of 2.8, 2.0 and 1.2, for PFOS, PFOA and PFBS, respectively. Deduced log K_{OC} values were lower than those of other persistent organic pollutants of similar hydrophobicity, such as lindane, chlordecone or pentachlorobenzene.

- Sorption parameters (K_d, K_F) of PFCs correlated well with their respective K_{OW}, thus confirming that the hydrophobicity of PFOS (log K_{OW} = 5.3), PFOA (log K_{OW} = 4.6) and PFBS (log K_{OW} = 2.7) was the driving force for their sorption in sludges and soils.

- Desorption isotherms of PFCs in sludges and soils also followed a linear pattern. Desorption parameters were systematically higher than the corresponding sorption parameters thus indicating a significant degree of irreversible sorption, which decreased in the sequence: PFOS > PFOA > PFBS.

- Desorption yields of PFOS in sludge and soil samples were lower than 4% and 13%, respectively, which confirmed that this compound was irreversibly sorbed. In addition to this, PFOA and PFBS were desorbed in higher rates (up to 27% and 60%, in sludges and soils, respectively), once again confirming that the physicochemical characteristics of PFCs, basically their hydrophobicity, controlled their sorption behaviour in these environmental matrices.