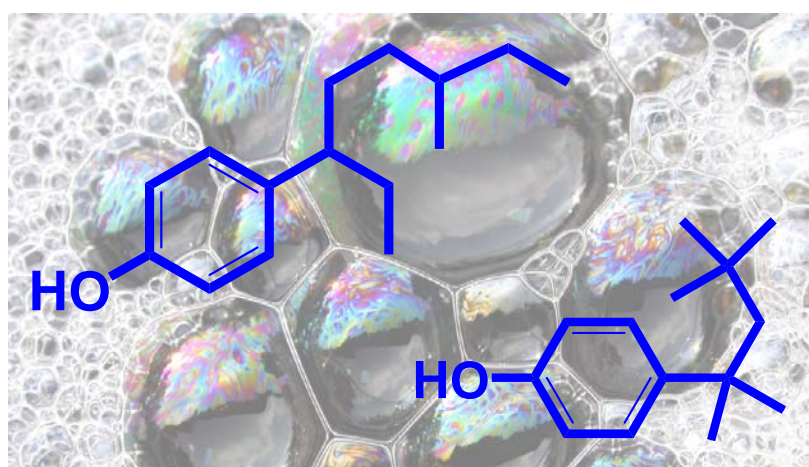


CAPÍTOL 5:

Comportament dels alquilfenols



5.1.- Problemàtica dels alquilfenols	237
5.2.- Degradació dels alquilfenols	240
Article científic 8: <i>Degradation of Nonylphenol, Octylphenol and Diazinon in Natural samples from the Ebro River Basin, studied by gas chromatography coupled to mass spectrometry (GC-MS)</i>	243
5.3.- Sorció dels alquilfenols	253
Article científic 9: <i>Sorption of alkylphenols on Ebro River sediments: Comparing isotherms with field observations in river water and sediments</i>	257
5.4.- Discussió addicional als articles	269

5.1.- Problemàtica dels alquilfenols

Els APs són compostos xenobiòtics que s'utilitzen en la manufactura d'antioxidants, resines fenòliques, polímers i additius per a olis lubricants però sobretot, en més d'un 65%, per a la producció dels APEOs (USEPA, 1990). Els APEOs són surfactants amb un rendiment excepcional i, conseqüentment, tenen un ús molt estès com a detergents, emulsionants, agents humitejants i dispersants, agents antiespumants i solubilitzants en aplicacions industrials (paper, tèxtil, formulacions de pesticides, combustibles, metalls i plàstics entre altres), comercials i domèstiques (Langford et al., 2002).

Els APEOs comercials més significatius són bàsicament els nonilfenols etoxilats (NPEOs, de l'anglès *nonylphenols ethoxylates*) i en un segon terme els octilfenols etoxilats (OPEOs, de l'anglès *octylphenols ethoxylates*). De fet els NPEOs suposen un 80% de la totalitat dels APEOs produïts mundialment i conseqüentment el NP és l'alquilfenol més utilitzat per a la manufactura d'APEOs (Ying et al., 2002). Des de que el NP es va sintetitzar per primer cop el 1940, el seu ús i fabricació s'han incrementat de forma quasi exponencial (Manzano et al., 1998). La producció anual de NP va arribar a 154.200 Tm a USA (Anònim, 2001), 73.500 Tm a Europa (HELCOM, 2002), 16.500 Tm al Nippon (JEM, 2001) i 16.000 Tm a Zhōngguó (Xina) (Anònim, 2004), de les quals un 60% van acabar al medi aquàtic (Renner, 1997). Degut a aquest ús extensiu dels APEOs, els OPEOs però sobretot els NPEOs entren a les EDARs en quantitats considerables. Allà es degraden de forma incompleta a APEOs de cadena curta i en últim terme a NP i OP (Ahel et al., 1994). Per això la major font d'APs al medi és la descàrrega d'efluents de les EDARs (Ahel et al., 1994; Petrovic et al., 2002b; Fries et al., 2003; Langford et al., 2005) i per tant el medi aquàtic suposa la ruta d'exposició principal per als humans i la fauna salvatge (Ying et al., 2002). Aquests compostos posseeixen l'habilitat d'imitar les hormones naturals interaccionant amb l'estrogen receptor (Jobling et al., 1993).

La preocupació va sorgir per primer cop el 1983-84 quan Giger i els seus col·laboradors de Suisse van establir que els NPEOs de cadena curta i els productes de degradació eren més tòxics per a la vida aquàtica que els seus precursors (Giger et al., 1984). A partir d'aquí es van descobrir

diversos efectes adversos provocats pel NP, tant com a disruptor endocrí com interferint en els sistemes reguladors de diferents tipus de cèl·lules:

~ Indueix la proliferació de cèl·lules tumorals en els pulmons (*Soto et al., 1991*).

~ Imita l'hormona natural 17β -estradiol competint pels llocs d'unió del receptor de l'estrogen natural degut a les seves similituds estructurals (*White et al., 1994*). Ja que aquest és un dels problemes més preocupants, s'han realitzat molts estudis i alguns dels efectes observats són:

- Va induir la producció de proteïnes femenines a truita (*Oncorhynchus mykiss*) a concentracions de $20,3 \text{ mg L}^{-1}$ (*Jobling et al., 1996*).
- La fertilitat masculina del peix *Xiphophorus maculatus* es va veure afectada negativament per concentracions de NP de $0,96 \text{ mg L}^{-1}$ després de 4 setmanes d'exposició (*Kinnberg et al., 2000*).
- Els efluent d'una EDAR que contenia un 10% de les aigües provinents d'una indústria tèxtil van demostrar la inducció de la producció de vitalogenina en truita de riu 5 km aigües avall del punt de descàrrega (*Sheahan et al., 2002*).
- Es va establir la correlació entre la producció de vitalogenina i anormalitats en les gònades de mascles de carpa i la presència de APs als rius que rebien efluent de les EDARs ($r^2 = 0,83$) (*Petrovic et al., 2002b*). Es van detectar anormalitats en mascles de carpa aigües avall de l'EDAR de Zaragoza degut a l'increment de vitalogenina plasmàtica, nivells baixos de testosterona i alteracions històriques en gònades suggerint la presència de xenoestrògens a l'aigua de riu (*Lavado et al., 2004*).
- La polvorització d'un insecticida amb NP com agent dispersant en un bosc va fer créixer la població de salmons que van tornar al riu, probablement per desencadenar un augment de la seva mortalitat (*Fairchild et al., 1999*).

~ És capaç de provocar toxicitat respiratòria de les cèl·lules, probablement canviant la permeabilitat de la membrana de la mitocondria a EC_{50}^* de $1,8 \text{ mg L}^{-1}$ (*Argese et al., 1994*).

* EC_{50} : és la concentració necessària per a produir efectes nocius a la meitat de la població estudiada

~ Incrementa la proliferació de cèl·lules de les glàndules mamàries a dosis de 0,01 mg d⁻¹ (Colerangle et al., 1996).

~ Altera les cinètiques del cicle cel·lular per conversió d'estructures immadures a altres madures (Colerangle et al., 1996).

~ Produeix associacions telemètriques i aberracions cromosòmiques (Roy et al., 1998).

~ Té activitat antiandrogènica, és a dir, és capaç d'interferir en l'òptim funcionament dels andrògens, que són essencials per al desenvolupament normal dels mascles i dels seus sistemes reproductius (Lee et al., 2003).

~ Té efectes adversos en el transport de calci del sarcoplasma reticular a la resta de cèl·lules de l'esquelet, amb un IC₅₀* de 880-2420 mg L⁻¹ (Kirk et al., 2003).

~ Inhibeix el creixement i la diferenciació de les cèl·lules neuronals i indueix la mort cel·lular a concentracions de més de 660 mg L⁻¹ (Kudo et al., 2004).

Freqüentment les concentracions en les que es dona un efecte advers en el medi o en l'home estan per sobre de les concentracions de NP trobades al medi ambient, però això no vol dir que el NP no estigui implicat en aquest tipus d'efectes, ja que al medi existeix més d'un factor o contaminant que pot afectar negativament els organismes. En el cas dels xenoestrògens s'ha demostrat en diversos estudis que l'efecte de 2 o més compostos amb capacitat de disrupció endocrina, fins i tot a concentracions baixes, pot ser additiva o sinèrgica (Kwack et al., 2001; Rajapakse et al., 2002).

Degut a aquestes i altres observacions, els països europeus van començar a emprendre accions contra els APs. Primer amb la introducció voluntària d'acords entre la indústria i els governs per a reduir l'ús i la producció dels derivats de NP (PARCOM, 2000). Seguidament els APs i els seus etoxilats es van incloure a la llista de substàncies prioritàries de la DMA (European Council, 2000) i a més a més molts dels usos del NP estan actualment regulats per la Directiva 2003/53/CE (European Council, 2003). Per altra banda, actualment l'EPA ha acceptat els riscos

*IC₅₀: és la concentració necessària per a produir un 50% d'inhibició del mecanisme estudiat

deguts a la presència del NP i ha preparat una guia sobre la qualitat del medi ambient aquàtic que recomana concentracions de NP en aigües de riu per sota de $6,6 \mu\text{g L}^{-1}$. Tot i això, molt països, incloent la *Zhōngguó* (Xina), *Bhārat* (Índia) i alguns països sud americans, produeixen i utilitzen APEOs en grans quantitats i no s'ha pres cap acció per a reduir o eliminar el seu ús (Soares et al., 2008). Actualment, a la major part d'Europa, *Canada* i *Nippon* els NPEOs s'estan substituint per altres surfactants com els alcohols etoxilats, que tot i que són menys eficients són molt més segurs per al medi gràcies a la seva ràpida degradació (Campbell, 2001).

En el cas de la conca de l'Ebre es van trobar concentracions d'APs en aigües i sediments pràcticament a tots els punts de presa de mostra. Aquestes concentracions van ser més elevades que per als altres compostos, puntualment de fins a $25 \mu\text{g L}^{-1}$ en aigua i 6.000 ng g^{-1} en sediments, concentracions que en el cas de l'aigua van superar els nivells que recomana l'EPA. Degut a aquests resultats reiteratius, obtinguts durant les 6 campanyes de presa de mostra a la conca de l'Ebre, i al fet que el destí d'aquests compostos al sistema aigua-sediment està menys estudiat, es va decidir fer un estudi del seu comportament, centrant-nos bàsicament en els aspectes de degradació i adsorció/absorció, ja que per a poder avaluar els riscos associats a qualsevol substància és necessari entendre la seva distribució i destí al medi (Ying et al., 2002).

5.2.- Degradació dels alquilfenols

La degradació és el procés de descomposició d'un compost químic en substàncies més simples. En general, els processos de degradació presenten una gran variabilitat i, sobretot en aquelles molècules més grans, consten de molts passos abans d'arribar a la mineralització completa, que freqüentment dona lloc a diòxid de carboni o metà. Són per tant uns processos clau per avaluar l'atenuació natural de contaminants al medi. Moltes vegades, però, els productes entremitjos de la degradació poden ser més tòxics que els precursors així com més difícils de degradar. La degradació es pot donar per diversos mecanismes, com la degradació química, fotodegradació o hidròlisi, i la biodegradació. La biodegradació, que en el medi és una de les més comuns, es defineix com la degradació natural de substàncies orgàniques per l'acció metabòlica o enzimàtica dels microorganismes. Hi ha dos grans tipus de biodegradació segons les condicions del medi:

- **Aeròbica:** es dona en presència d'oxigen i els organismes que la causen són aerobis. En general és molt completa i allibera molta energia, en forma de diòxid de carboni i aigua.
- **Anaeròbica:** es dona en absència d'oxigen i els organismes que la causen són anaerobis. Són oxidacions incompletes i alliberen menor quantitat d'energia en forma de metà.

En principi qualsevol compost natural es pot descompondre biològicament. En canvi molts dels compostos químics són difícilment degradables per microorganismes, ja que en molts casos no tenen la bateria enzimàtica capaç de fer-ho. Aquests són els compostos no biodegradables, que es poden anar acumulant a sòls i sediments o als teixits grassos dels organismes, un exemple serien els pesticides organoclorats (*Grimalt et al., 1994*). D'aquesta manera augmenta la seva concentració a mesura que s'avança per la xarxa tròfica cap a nivells superiors donant lloc a bioamagnificació. Per a conèixer el destí d'un contaminant al medi és per tant necessari conèixer la seva degradació, ja sigui en forma de biodegradació, fotodegradació o altres mecanismes d'atenuació al medi.

Els processos de degradació es poden descriure matemàticament amb una única equació que engloba els diferents passos de la reacció. D'aquesta manera no es revela el mecanisme que té lloc sinó que només permet calcular l'atenuació del compost com a resultat de la suma dels diversos tipus de degradació (*Schwarzenbach et al., 2003*). L'equació més senzilla amb la que es pot caracteritzar matemàticament un procés de degradació és la que descriu la cinètica de primer ordre:

$$C = C_0 \cdot e^{-kT_{1/2}}$$

on C (mg L^{-1}) és la concentració en el temps T (d), que també està en funció de la constant k (d^{-1}) i de la concentració inicial C_0 (mg L^{-1}). Un paràmetre molt utilitzat per comparar la velocitat dels processos de degradació per a diferents compostos és la vida mitjana ($T_{1/2}$), és a dir el temps necessari per a que la concentració inicial es redueixi a la meitat. En les cinètiques de primer ordre aquest temps és sempre independent de la concentració i es calcula com:

$$\frac{C_0}{2} = C_0 \cdot e^{-kT_{1/2}} \Rightarrow T_{1/2} = \frac{\ln 2}{k} = \frac{0,693}{k}$$

Respecte el cas que ens ocupa en aquesta tesi, es coneix que la biodegradació dels APEOs a les EDARs generalment comença amb un escurçament de la cadena etoxilada, que dona lloc a APs de cadena curta amb una o dues unitats etoxilades. La completa detoxilació amb formació d'APs només s'ha trobat a les EDARs sota condicions anaeròbiques (Giger *et al.*, 1984). Els percentatges descrits d'eliminació de NPEOs a EDARs de diversos països varien entre 37 i 99% (Di Corcia *et al.*, 1994; Crescenzi *et al.*, 1995; Naylor, 1995; Nasu *et al.*, 2001; Céspedes *et al.*, 2008). Aquest procés genera per tant gran quantitat de NPEOs de cadena curta (mono o dietoxilats) i de NP que s'aboquen al medi. A les EDARs d'USA molts dels efluent van presentar alts nivells de NP (fins a 978 $\mu\text{g L}^{-1}$) i de NPEOs (fins a 33.700 $\mu\text{g L}^{-1}$). El procés de degradació primària dels APEOs que es dona a les EDARs s'ha estudiat àmpliament en diverses matrius, com per exemple en aigua de riu, aigua de mar, sediments i sòls, on s'han trobat un ampli rang de constants de degradació (Yoshimura, 1986; Manzano *et al.*, 1999; Potter *et al.*, 1999). La major part d'aquests estudis, però, només es centren en la degradació que suposa la pèrdua de la cadena etoxilada, i no investiguen la degradació posterior del NP i l'OP.

En aquesta tesi es pretenia aprofundir més en el procés de degradació d'aquests compostos, de forma que es va dissenyar un estudi de degradació simultània dels dos APs, en el que es va incloure també el pesticida diazinon, ja que és un dels pocs que es van trobar tant en aigües com en sediments. En aquest estudi es va intentar reproduir el medi aquàtic amb una combinació d'aigua i sediments provinents del punt R19, corresponent al riu Ebre a Amposta. Així mateix es van provar diferents condicions per a intentar discernir entre la influència dels processos de fotodegradació i biodegradació aeròbica i anaeròbica. Els resultats obtinguts es recullen a l'article científic 8, reproduït a continuació.

Article científic 8

Degradation of nonylphenol, octylphenol and diazinon in the Ebro River water-sediment system

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Enviat a Chemosphere

Degradation of nonylphenol, octylphenol and diazinon in the Ebro River water-sediment system

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ABSTRACT

In this study we have evaluated the degradation kinetics of octylphenol (OP), nonylphenol (NP) and the pesticide diazinon in water and sediments, simulating environmental conditions with different oxygen and light conditions. These compounds have been chosen given their ubiquity in the aquatic Ebro ecosystem. After incubation of samples for 70 days, it has been found that diazinon is degraded in more than 95%, followed by OP with percentages of elimination between 65 and 92%, while NP was the most recalcitrant of the three compounds with degradation of 47-64% of the initial concentration. The degradation kinetics and processes varied within the different conditions and compounds, being aerobic biodegradation the main process in eliminating diazinon both from water and sediment. For OP and NP, photodegradation contributed more than biodegradation to its decay during the experiment. Among oxygen conditions for these two compounds, different but not statistically significant half lives were observed, with aerobic conditions leading to slightly higher degradability. The degradation study was followed using gas chromatography coupled to mass spectrometry.

Keywords: alkylphenols, diazinon, degradation, water, sediment

1. Introduction

Alkylphenols (APs) are a group of compounds used in the manufacture of antioxidants, phenolic resins, polymers and lubricating oil additives (Soares et al., 2008) but mainly, in more than 65%, for the production of alkylphenol ethoxylates (APEOs) (USEPA, 1990). APEOs are surfactants with exceptional performance and consequently they are used widely as detergents, emulsifiers, wetting and dispersing agents, antistatic and antioxidants in commercial, domestic and industrial applications (paper, textile, pesticide formulations and plastics among others) (Langford and Lester, 2002). The most widely used commercial APEOs are nonylphenol ethoxylates (NPEOs) and octylphenol ethoxylates (OPEOs). In fact NPEOs account for about 80% of worldwide APEOs production (Ying et al., 2002) and consequently nonylphenol (NP) is the AP most used in the manufacture of APEOs. Since NP was first synthesized in 1940, its use and production has increased almost exponentially (Manzano et al., 1998) although now has been prohibited in Europe in pesticide formulations at concentrations higher than 0.1% (European Council, 2003). The annual production of NP reached 154.200 Tm in USA (Anonymous, 2001), 73.500 Tm in Europe (HELCOM, 2002), 16.500 Tm in Japan (JEM, 2001) and 16.000 Tm in China (Anonymous, 2004), from which, 60% reached the aquatic environment (Renner, 1997). Once in the aquatic ecosystem, APEOs are metabolized in fish and higher organisms (Porte et al., 2006) although they can produce effects due to the continuous exposure (Solé et

al., 2000). At the same time, they can remain soluble in water (Sánchez-Avila et al., 2009) or adsorbed to sediments (Navarro et al., 2009a) where they are incompletely degraded to short chain APEOs and finally to NP and OP (Ahel et al., 1994). These compounds may persist for a longer time due to their continuous input and the low photochemical and hydrolytic degradability. As a result, a great concern has arisen due to their ubiquity in environment and to their well demonstrated endocrine disrupting properties (Jobling and Sumpter, 1993).

Several studies have been performed to evaluate the degradability of APEOs (de Voogt et al., 2000; Destailats et al., 2000; Inoue et al., 2003; La Guardia et al., 2001; Liu et al., 2008; Staples et al., 2001) but little is known on the fate of NP and OP in the aquatic ecosystem. Within a Wastewater Treatment Plant (WWTP), cleavage of the ethoxy chain of APEOs release short chain APs with one or two ethoxy units while under anaerobic conditions NP and OP are generated (Giger et al., 1984). Removal rates vary widely according to the WWTP (Ying et al., 2002) but in any case WWTP may be responsible of a continuous input to receiving waters (Cespedes et al., 2008). In river water the biodegradation of NPEOs vary from 68% to 96% with different temperature conditions (Manzano et al., 1999). Potter et al. (Potter et al., 1999) studied also the degradability in seawater and found similar results. Once accumulated in sediments, APEOs can also be aerobically and anaerobically degraded to short chain APEOs containing one or two ethoxy units, with half lives of less than 10 days (Yoshimura, 1986).

However, most of the degradation studies are based in the desethoxylation of APEOs and little is known on the real fate of APs in the aquatic ecosystem.

The present study tries to focus on the fate of APs in the Ebro river aquatic system. It has been recently shown that the whole Ebro river (910 km) contains high concentrations of OP and NP both in water (up to $25 \mu\text{g L}^{-1}$) and in sediment (up to 6.000 ng g^{-1} -dry weight) due to the intense human pressure along the basin (Navarro et al., 2009b; Navarro et al., 2009c). Also, the pesticide diazinon was found iteratively along the basin. In a first study to evaluate the fate of APs, we studied the sorption of OP and NP using Ebro river sediments collected at the source, middle and mouth of the river. It was demonstrated that APs are adsorbed at the concentrations found in the river and it was possible to correlate the sorption constants with the Total Organic Content (TOC) of the sediments. Thus, sediments become a sink for this class of pollutants. Following this finding, we were particularly interested in determining the degradability of APs in water and sediments to better establish the partitioning among these matrices and contribute to evaluate the potential effect of APs in river waters (Ying et al., 2002). Thus, the objectives of the present study were: (i) to study the degradation kinetics of OP, NP and diazinon in Ebro river water and sediment simulating Ebro conditions; (ii) to establish the half life of each compound in different conditions of light and oxygen and (iii) to evaluate the importance of photodegradation and biodegradation processes for the elimination of these compounds. For such purpose, an internal standard (anthracene-D10) at $100 \mu\text{g mL}^{-1}$ in samples were spiked at environmental relevant concentrations, incubated during 70 days and sediments and waters were analyzed throughout this period using mass spectrometric techniques.

2. Experimental

2.1. Chemicals

Nonylphenol technical mixture (92% purity) and diazinon (99% purity) were purchased from Riedel de Haën (Seelze, Germany), 4-tert-Octylphenol (97% purity) was purchased from Supelco (Bellefonte, PA, USA). Single isotopically labeled surrogates (atrazine-D5 and nonylphenol-D8) at $100 \mu\text{g mL}^{-1}$ in acetone and cyclohexane were from Dr. Ehrenstorfer (Augsburg, Germany). The chemical structures of the compounds used in this study and some of their chemical properties are presented in Table 1. Standard working solutions were diluted from the commercial ones in hexane. SPE extraction cartridges Oasis HLB 60 mg 3 cc were from Waters (Milford, MA USA). Florisil powder was of 0.150-0.250 mm for residue analysis quality from Merck (Darmstadt, Germany), baked at $150 \text{ }^\circ\text{C}$ over night to ensure dryness. Hydromatrix was from Varian (Palo Alto, CA USA). Methanol and water at HPLC grade and GC grade dichloromethane (DCM), ethyl acetate (EtAc) and hexane (Hex) were purchased from

Merck (Darmstadt, Germany). Nitrogen of 99.995% purity used as drying stream was from Air Liquide (Paris, France).

2.2. Sample collection

Water and sediments were taken from the Ebro river at Amposta (lower course, R19 of AquaTerra sampling) sites (Navarro et al., 2008) in march 2006. Water from 0.5 m under the surface was sampled from a bridge using a stainless steel grab with an amber glass bottle placed inside. At this same site, surface sediments (10 cm upper layer) were taken from the shore using a Van Veen grab. Samples were stored and transported refrigerated to the laboratory. Immediately after collection, sediments were air-dried overnight and sieved at $500 \mu\text{m}$ to obtain a homogeneous mixture. Water was used unfiltered. The total organic carbon of the samples was 1.9 mg L^{-1} for water and 2.3% for the sediment.

2.3. Experimental design

Batch experiments were performed using 2.5 L glass bottles containing 250 g of sieved sediment and 2.5 L of water, to which we added 0.05 mg L^{-1} of the mixture of the three studied compounds. Two kinds of bottles were used: colourless bottles that caused less than 5% reduction of the natural radiation of the visible spectrum and amber bottles that caused more than 80% reduction of this radiation. In each type of bottle aerobic and anaerobic conditions were used. For the aerobic conditions, the bottles were stirred daily and for anaerobic conditions the bottles were bubbled with N_2 for 20 min every time that the bottle was opened. The combination of these parameters generated four different degradation conditions that were carried on in duplicates. The bottles were closed and incubated outdoor at ambient temperature and exposed to sunlight, simulating natural field conditions. In these experimental set-up the losses due to sorption to glass and cap and volatilization were equal to 10% for all conditions and were not considered to compare the degradation rate constants of each condition. The experiment was conducted between 21st of March and 31st of May 2006. During the experiment, temperature and solar radiation were recorded at a local meteorological station (Generalitat de Catalunya, 2006). The average total daily radiation of this period was 233 W m^{-2} and the mean daily temperature was $16.5 \text{ }^\circ\text{C}$. The experiment lasted 70 days during which 16 water and sediment samples were taken at days 0, 1, 2, 5, 7, 9, 12, 16, 21, 27, 33, 41, 48, 55, 62, 70. At each sampling time, 25 mL of water and 5 g of sediments were collected. These amounts supposed a reduction of 16% and 32% respectively of the initial amount of water and sediment samples.

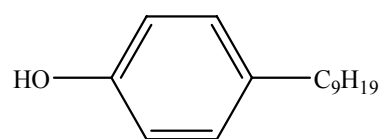
2.4. Analytical methodology

Water and sediment extraction and analysis were

performed as described in Navarro et al. (Navarro et al., 2009b) and Navarro et al. (Navarro et al., 2009c) respectively. Atrazine-D5 and nonylphenol-D8 were added as surrogate standards to 25 mL of water at $0.2 \mu\text{g L}^{-1}$. These samples were extracted using Oasis HLB SPE cartridges, which were firstly conditioned by gravity with 5 mL of DCM:EtAc (1:1), 5 mL of Hex:DCM (1:1), 1 mL of methanol and 1 mL of water. Then, samples were percolated using a Baker Vacuum system from J.T. Baker (Phillipsburg, NJ USA) at a flow

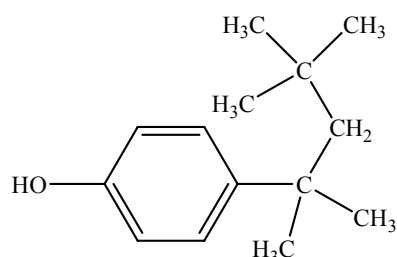
rate of 6 mL min^{-1} . Afterwards, cartridges were rinsed with 2 mL of HPLC water to remove matrix interferences, dried under vacuum for 20 min to remove water and immediately after eluted with 5 mL Hex:DCM (1:1) and 3 mL DCM:EtAc (1:1) followed by 2 mL of pushing air, all at a rate 1 mL min^{-1} using an automated ASPEC XL system from Gilson (Middleton, WI USA). These extracts were evaporated with a Reacti-Vap III from Pierce (Rockford, IL USA) operating under a gentle stream of nitrogen.

Table 1 Chemical structures and properties of 4-NP, 4-tert-OP and Diazinon



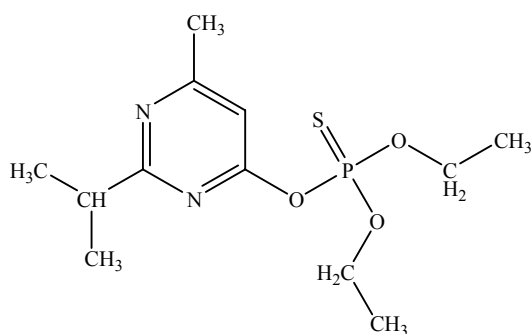
4-nonylphenol (84852-15-3)

Vapor pressure 25 °C: 12.56 mPa
Henry constant: $4.36 \times 10^{-1} \text{ Pa m}^3 \text{ mol}^{-1}$
Solubility: 5.43 mg L^{-1}
Log K_{ow}: 4.48



4-tert-octylphenol (140-66-9)

Vapor pressure 25 °C: 63.72 mPa
Henry constant: $6.98 \times 10^{-1} \text{ Pa m}^3 \text{ mol}^{-1}$
Solubility: 12.6 mg L^{-1}
Log K_{ow}: 4.12



Diazinon (333-41-5)

Vapor pressure 25 °C: 12.00 mPa
Henry constant: $6.09 \times 10^{-2} \text{ Pa m}^3 \text{ mol}^{-1}$
Solubility: 60 mg L^{-1}
Log K_{ow}: 3.30

Sediment samples were freeze-dried during 48 hours at -40 °C and under a 10^{-2} mbar vacuum. One gram of each sample was spiked with the surrogate solution at $125 \mu\text{g kg}^{-1}\text{-dw}$ and extracted using the pressurized liquid extraction (PLE) system ASE 200 from Dionex (Sunnyvale, CA USA). The mixture hexane:dichloromethane (1:1) was used as extraction solvent. This system was optimized to perform the extraction and clean-up within the ASE cell in a single step, including Florisil inside the ASE cell (Hildebrandt et al., 2007). For the extraction step, 22 mL ASE stainless steel cells were packed as follows: 2 g of clean-up powder were placed at the outflow side of the cell and other 5 g were mixed with the sample. The

remaining space was filled with pressed hydromatrix. Extraction was performed with a mixture of hexane:dichloromethane (1:1) and using a heat-up time of 5 min, a temperature of 100 °C and at 1500 psi ($1 \text{ psi} = 6894.76 \text{ Pa}$). The solvent flow was of 60% and two cycles of extraction were performed with 10 min in static mode. The purge time was of 90 s with nitrogen gas. Extracts were evaporated at room temperature to nearly dryness using a TurboVap LV from Caliper LifeSciences (Hopkinton, MA USA).

Both water and sediments extracts were reconstituted into glass amber vials for gas chromatography. The final samples were spiked with anthracene-D10 at a concentration of $160 \mu\text{g L}^{-1}$ and the

final volume was adjusted to 75 μL and 250 μL of hexane for water and sediment extracts, respectively.

2.5. Instrumental analysis

GC/MS analysis was performed with a gas chromatograph Thermo Electron (San Jose, CA USA) model Trace 2000 coupled to a mass spectrometer from Thermo Electron. The mass spectrometer was operated in the electron impact ionization mode with an ionizing energy of 70 eV. Compound separation was achieved using a capillary column HP-5MS of 15 m x 0.25 mm i.d. with 0.25 μm film thickness from J&W Scientific (Folsom, CA USA) with the temperature program: from 60 $^{\circ}\text{C}$ to 145 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C min}^{-1}$ to 165 $^{\circ}\text{C}$ at 6 $^{\circ}\text{C min}^{-1}$ to 180 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C min}^{-1}$ and finally to 325 $^{\circ}\text{C}$ at 25 $^{\circ}\text{C min}^{-1}$ (holding time 2 min). Injection was achieved in the splitless mode keeping the split valve closed for 0.8 min. Helium was used as carrier gas at a flow of 1.2 mL min^{-1} . The injector, transfer and ion source temperatures were set at 280 $^{\circ}\text{C}$, 250 $^{\circ}\text{C}$ and 200 $^{\circ}\text{C}$ respectively. Acquisition was performed in scan mode from 80 to 300 amu. Identification and quantification were carried out automatically by the Xcalibur software.

2.6. Study of degradation kinetics

The NP, OP and diazinon data collected for this study fitted well with first-order kinetics: $C = C_0 e^{-kt}$, where C_0 is the initial concentration, C is the concentration at a given time period (t) and k is the degradation rate constant. The remaining percentage was calculated as the compound residue concentration divided by the original concentration. The half-lives were also calculated to compare the speed of the degradation processes: $t_{1/2} = \ln 2 k^{-1} = 0.693 k^{-1}$

3. Results and discussion

We compared the degradation rates of OP, NP and diazinon incubated under laboratory conditions trying to simulate environment ones. Given that photodegradation and biodegradation are the main processes driving to the elimination of these compounds in the environment, we tested two oxygen and light conditions. For all compounds, degradation followed a first order kinetics reaching a steady state after the 70 days of incubation. Water and sediment degradation isotherms for colourless bottle and aerobic conditions are plotted in fig. 2 for each of the three studied compounds. In all the cases the equilibrium due to partitioning processes between water and sediments was achieved after 5 days of incubation. After this period the concentration found in the sediment remained within less than 20% variation between $t = 0$ days and $t = 70$ days (Figure 1). Therefore the isotherm corresponding to the water matrix was considered as representative of the attenuation of the whole lab scale environment created to simulate the natural conditions and from here on all the showed results correspond to the water phase.

The degradation rates in water were diazinon > OP > NP, following the steeper isotherms and lower remaining percentage of the corresponding compound after the 70 days of incubation (Figure 1). The higher the water solubility and polarity of the compound, the higher the partitioning into water and the higher degradability as it was not sorbed in the sediment. This situation was observed in a previous sorption study considering OP and NP (Navarro et al., 2009a) that reported stronger sorption for NP than for OP.

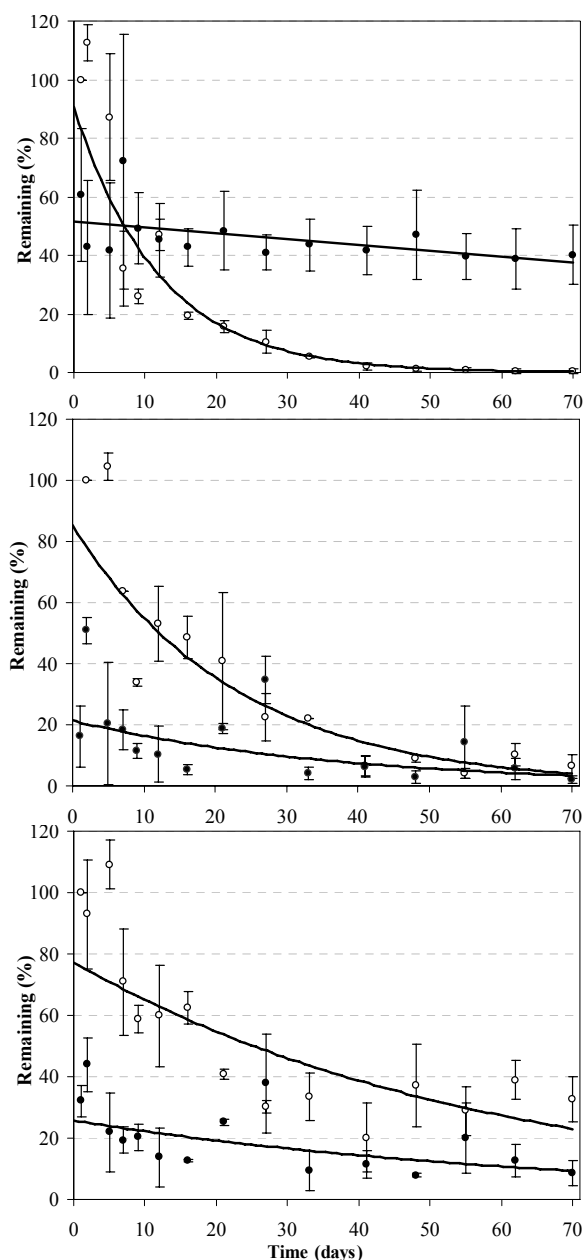


Figure 1. Remaining percentage of diazinon (a), OP (b) and NP (c) for water (○) and sediment (●) samples in the case of colourless bottle and aerobic conditions

The scheme shown in Fig. 1 for colourless bottle and aerobic conditions was similar for the other 3 conditions tested and all degradation parameters for the

water phase for the four conditions tested are indicated in Table 2. The degradation rates and half-lives showed some differences according to the incubation conditions. Diazinon had lower half-live times in aerobic conditions, while the amount of radiation did not affect the degradation process. Half-lives of 8 days for the high oxygen concentration and of 14 days for anaerobic conditions were estimated, with no differences according to the light incidence. After the 70 days that the experiment lasted, diazinon in water was completely degraded in water and no differences were observed between the theoretical elimination rate and the real one.

On the other hand, both NP and OP in water showed a lower degradation rate than diazinon and degradation rates were affected more by the amount of radiation than by the amount of oxygen. Specially, OP degraded at double rate in colourless bottles than in amber bottles (Table 2) while for NP light increased the degradation in 32%. This same observation was found for anaerobic conditions. According to the standard deviation among duplicates, oxygen did not contribute significantly to the degradability of OP and NP. Differing

from diazinon, the degradation process was much slower for APs and elimination was not completed after the 70 days of incubation. For OP in colourless bottles and in aerobic conditions, 92% of the initial amount was degraded while in the amber bottle this percentage was reduced to 65%, values similar to those obtained in anaerobic conditions. Calculated and real elimination rates did not differ significantly. For NP the picture was somewhat different and the real elimination rate varied from 64 and 47% in the conditions tested while the theoretical value according to the kinetic constants was between 67 and 81%. A part of the lack of fit with the values of the real and theoretical elimination of NP, a big difference in the scheme was also observed. While the theoretical elimination, in concordance with the half-live, showed similar degradation on aerobic and anaerobic colourless bottles, the real elimination showed a similar degradation, between 47 and 51%, for amber aerobic and anaerobic conditions but also for colourless anaerobic conditions. This lack of concordance indicates that for NP the process is also influenced by the aerobic biodegradation, in combination with photodegradation.

Table 2 Degradation rate constants and percentage of elimination of diazinon, NP and OP under different conditions

	Oxygen conditions	Bottle	Equation	t _{1/2} (day)	r ²	Real % elimination	Theoretical % elimination
Diazinon	Aerobic	Colourless	77.58e-0.11t	8.2	0.93	99	100
	Aerobic	Amber	51.58e-0.10t	8.7	0.92	98	100
	Anaerobic	Colourless	64.39e-0.06t	14.1	0.95	99	99
	Anaerobic	Amber	53.81e-0.06t	14.5	0.96	95	98
NP	Aerobic	Colourless	3.59e-0.02t	28.3	0.71	64	80
	Aerobic	Amber	3.34e-0.02t	41.9	0.78	51	68
	Anaerobic	Colourless	2.93e-0.02t	30.2	0.88	47	81
	Anaerobic	Amber	2.77e-0.02t	44.7	0.92	48	67
OP	Aerobic	Colourless	14.02e-0.06t	15.2	0.88	92	98
	Aerobic	Amber	8.88e-0.02t	29.4	0.82	65	80
	Anaerobic	Colourless	9.90e-0.05t	17.0	0.94	91	97
	Anaerobic	Amber	8.03e-0.03t	30.3	0.87	79	82

Table 3 compiles bibliographic half lives of the target compounds in water, sediment or other matrices under different oxygen conditions. While the study realised here combines real environmental water and sediments into the same degradation experiment, the studies found in the literature consider mostly only a solid matrix or its combination with artificially prepared medium. For diazinon, the half life calculated in the presence of sediments is somewhat smaller than in a previous experiment using also Ebro river water but in the absence of sediment (Lacorte et al., 1995). This suggests that although aerobic conditions are main pathways for the elimination of this compound, sediment plays an important role in adsorbing part of this

compound which has an intermediate K_{ow} and thus a potential accumulating potential. Comparison of half lives of diazinon with those obtained in sediment showed larger values for freshwater and saltwater sediments than for the present study conditions that combines sediment and water. This fact confirms that the presence of the two matrices is necessary to achieve faster attenuation of diazinon in the environment. In any case faster degradation under aerobic condition than under anaerobic conditions appears both in this study and in the literature research. Apart from the half-live, the percentage of elimination achieved with the experiments using sediment or water and sediment is higher than 90% in all the cases showing the complete

degradation of this compound in sediment while in soil only a 25 and 62% of degradation was achieved.

For APs, reported half lives vary among different studies found in the open bibliography. Half lives in water are not reported for NP but the percentage of elimination shows less degradation of this compound when only seawater is considered (Ekelund et al., 1993). The situation is different for OP degradation in freshwater (Johnson et al., 2000) where degradation is found at a wide range of half-lives but in all the cases the final percentage of elimination reaches 100%, similarly to our results. All the studies performed only with the solid matrix both for OP and NP show no degradation under anaerobic conditions, indicating the importance of having a combination of water and solid matrix for the attenuation of APs in the environment

under these conditions. Half-lives reported in the studies using solid matrices are very variable, from 1.8 to 99 days for NP and in a narrower interval from 4.1 to 33 days for OP. In both cases these ranges cover also the half-lives found in the present study. The percentages of elimination reported in solid matrices (with the exception of the anaerobic ones that have been commented previously) reach values of 100% in most of the cases. The variability in the half lives found in this comparison can be attributed to the different matrixes used as well as to the differences on the performance of the experiments, consequently any of these rates can be directly assumed into the environment but the tendencies and relations between different conditions and compounds are useful to approach the behaviour of these compounds in the environment.

Table 3 Data compilation of $T_{1/2}$ and % of elimination from laboratory studies under different conditions and matrices

	Matrix	Conditions	$T_{1/2}$ (days)	% elimination	Author
Diazinon	Estuarine water	Aerobic	10.6	Not reported	(Lacorte et al., 1995)
	Freshwater sed.	Aerobic	14.4	100% after 110 days	(Bondarenko and Gan, 2004)
	Freshwater sed.	Anaerobic	31.7	90% after 110 days	(Bondarenko and Gan, 2004)
	Saltwater sed.	Aerobic	21.1	95% after 110 days	(Bondarenko and Gan, 2004)
	Saltwater sed.	Anaerobic	23.7	95% after 110 days	(Bondarenko and Gan, 2004)
	Soil	-	-	25% after 40 days	(Liyantage et al., 2007)
	Soil	Aerobic	-	61.9% after 98 days	(Fenlon et al., 2007)
NP	Seawater	Aerobic	-	40 % after 60 days	(Ekelund et al., 1993)
	Seawater	Anaerobic	-	20 % after 60 days	(Ekelund et al., 1993)
	Aquifer material	Aerobic	7	90 % after 70 days	(Ying et al., 2003)
	Aquifer material	Anaerobic	-	Unchanged over 70 d.	(Ying et al., 2003)
	Sediment	Aerobic	13.6-99	100 % after 28-70 d.	(Yuan et al., 2004)
	Sediment	Anaerobic	46.2-69.3	100 % after 63-84 d.	(Chang et al., 2004)
	Sludge	Aerobic	1.5-9.5	100 % after 21 days	(Chang et al., 2005b)
	Sludge	Anaerobic	23.9	85.5 % after 84 days	(Chang et al., 2005a)
	Aquifer material	Aerobic	1.8	100% after 8 days	(Ying et al., 2008)
	Aquifer material	Anoxic	-	Unchanged over 70 d.	(Ying et al., 2008)
OP	Freshwater	-	9.0-54.0	75-100% after 35 days	(Johnson et al., 2000)
	Soil	Aerobic	9-19	60-90% after 16 days	(Shibata et al., 2006)
	Soil	Anaerobic	-	Unchanged over 224 d.	(Shibata et al., 2006)
	Aquifer material	Aerobic	4.1	100% after 21 days	(Ying et al., 2008)
	Aquifer material	Anoxic	-	Unchanged over 70 d.	(Ying et al., 2008)
	Sludge	Aerobic	28.1	Not reported	(Liu et al., 2008)
	Sludge	Anaerobic	33.0	Not reported	(Liu et al., 2008)

4. Conclusions

The degradation kinetics of diazinon, OP and NP, 3 compounds widely distributed in water and sediments of the Ebro river, showed that they are eliminated in 50-100% from water within 70 days of exposure although complete elimination does not occur once sorbed to sediments. The half lives of diazinon were of 8 and 14 days in aerobic and anaerobic conditions, respectively, and light did not enhance degradation. Contrarily, both APs were degraded faster in the presence of light, while the oxygen content did not affect their degradability. Depending on the type of compound, multiple factors can affect the elimination rates of organic contaminants

and thus it is important to evaluate the main processes that might affect their fate and thus their bioavailability and potential toxic effects. Studies such as the one herein proposed try to simulate environmental conditions by using real samples, spiking at environmental relevant concentrations and incubating the solutions for a reasonable long period. Although the results cannot be extrapolated to field conditions, the data herein obtained can be used to assess the impact of compounds widely used in agricultural and industrial activities and also may serve to reflect on the sources and presence of these compounds in the river once it is known that their half lives are of several days to 1 month.

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5.3.- Sorció dels alquilfenols

Abans que res cal puntualitzar una qüestió terminològica. En l'article científic 9, i qualsevol altre article relacionat amb aquest tema, s'utilitza la paraula anglesa *sorption*, que engloba els processos d'adsorció (que es dona quan les molècules s'enganxen a una superfície) i absorció (que es dona quan les molècules penetren en una matriu tridimensional). Aquest terme resulta molt útil quan es desconeix el procés que està tenint lloc en un medi determinat. Però en català aquesta paraula no existeix i només es disposa dels mots adsorció i absorció per a definir els dos processos de forma individual. Utilitzar els dos noms resulta confús, especialment tenint en compte que a la discussió addicional s'inclou un petit apartat en el que es pretén discernir quin dels dos processos és el predominant. Per aquesta raó ens hem pres la llicència d'utilitzar la paraula sorció i els seus derivats sorbent i sorbat, com adaptació de l'anglès, tot i ser conscients que la seva utilització en català no està acceptada.

La sorció és un procés extremadament important perquè pot afectar de forma dramàtica el destí i els impactes del compostos químics al medi. Aquesta importància es deu a que molècules idèntiques es comporten de forma diferent si es troben a la fase gasosa, envoltades per molècules d'aigua o retingudes a la superfície o a l'interior d'un sòlid. Per això, el transport d'aquestes molècules també varia si estan en dissolució a l'aigua o adherides a partícules que poden sedimentar. Per altra banda, les molècules dissoltes tenen més facilitat per canviar de medi, de forma que la sorció pot afectar la biodisponibilitat d'un compost així com la seva biotransformació o toxicitat (*Schwarzenbach et al., 2003*). Per aquestes raons, l'associació dels contaminants amb les partícules aquàtiques és un dels processos importants que controlen el destí d'aquests compostos en rius i altres ambients aquàtics.

La sorció és la combinació d'interaccions que governen l'associació d'una substància química (anomenada sorbat) amb un sòlid o una barreja de sòlids (anomenat sorbent). Per a caracteritzar l'equilibri de distribució d'un compost químic entre els sòlids i la solució d'un medi aquàtic cal conèixer la concentració de sorbat en la solució, C_A , i la concentració de sorbat en el sorbent, C_S . La relació d'aquestes dues concentracions es coneix comunament com isoterma de sorció. El nom d'isoterma s'utilitza per a indicar que la relació de sorció només s'aplica a una temperatura constant. Les isoterms de sorció determinades experimentalment

exhibeixen una gran varietat de formes segons les interaccions que s'estableixen entre sorbats i sorbents, que acostumen a ser una barreja d'adsorció i d'absorció. El cas més simple és la isoterma lineal, en la que l'afinitat del sorbat pel sorbent roman igual al llarg del rang de concentracions considerat. En la major part dels casos, però, quan la concentració del sorbat augmenta resulta més complicat que les molècules quedin retingudes ja que els llocs de sorció es comencen a saturar reflectint un predomini de processos d'adsorció.

Una aproximació matemàtica per a l'ajust de dades experimentals de sorció utilitzant el mínim de paràmetres ajustables es basa en la relació empírica coneguda com isoterma de Freundlich:

$$C_S = K_F \cdot C_A^{1/n}$$

on C_S (mg kg^{-1}) i C_A (mg L^{-1}) són les concentracions en el sorbent i en l'aigua respectivament, que estan en funció de K_F , la constant de Freundlich o factor de capacitat ($(\text{mg kg}^{-1}) (\text{mg L}^{-1})^{-1/n}$), i $1/n$, l'exponent de Freundlich. Aquesta equació assumeix que hi ha múltiples tipus de llocs de sorció actuant en paral·lel, on cadascun d'ells té una energia lliure de sorció diferent. L'exponent és un índex de la diversitat de les energies lliures associades amb la sorció d'un solut a un sorbent heterogeni. Quan $1/n = 1$ la isoterma és lineal, del que es dedueix que les energies lliures són constants a qualsevol concentració del sorbat. Quan $1/n < 1$ la isoterma es cònca, de forma que a mesura que augmenta la concentració del sorbat la sorció és cada cop més difícil mentre que quan $1/n > 1$ la isoterma és convexa, indicant que la sorció es veu afavorida quan augmenta la concentració de sorbat. K_F i $1/n$ es poden deduir de les dades experimentals amb una regressió lineal en la forma logarítmica de l'equació anterior:

$$\log C_S = \log K_F + 1/n \cdot \log C_A$$

Si la isoterma no es pot descriure amb l'equació de Freundlich és perquè les assumpcions que aquesta considera no són vàlides per al cas estudiat, per exemple quan s'arriba a concentracions en les que els llocs de sorció arriben a saturar-se. En aquests casos existeixen altres aproximacions, com la isoterma de Langmuir, que es poden ajustar millor al model. En general, però, la primera aproximació que s'utilitza és l'equació de Freundlich per ser la més senzilla i fàcil d'interpretar. Aquesta isoterma també és la que es va utilitzar en aquesta tesi, obtenint en tots els casos bons coeficients de regressió.

Per tal de fer l'estudi de sorció dels APs previst per a millorar la seva caracterització es va fer una estada de 7 mesos als laboratoris del *Zentrum für Angewandte Geowissenschaften* (Centre de Geociències aplicades) de la *Eberhard Karls Universität Tübingen (Deutschland)* sota la direcció del Dr. Tilman Gocht, el Dr. Johannes Barth i el Dr. Peter Grathwohl. Aquest grup té una prolongada experiència en processos de sorció, tal i com es veu reflectit en les seves nombroses publicacions sobre aquest tema (*Grathwohl et al., 1997; Kleineidam et al., 1997; Karapanagioti et al., 1999; Setarge et al., 1999; Rahman et al., 2000; Grathwohl et al., 2002; Kleineidam et al., 2002; Bold et al., 2003; Kleineidam et al., 2004; Rahman et al., 2004; Abelman et al., 2005; Wang et al., 2007; Endo et al., 2008a; Endo et al., 2008b; Razzaque et al., 2008; Yang et al., 2008*). Durant aquesta estada es van fer diversos experiments de sorció d'APs utilitzant com a sorbents tres sediments diferents de la conca de l'Ebre així com altres materials orgànics. Els resultats obtinguts per als sediments estan recollits a l'article científic 9, que es reproduïx a continuació.

Article científic 9

Sorption of alkylphenols on Ebro River sediments: Comparing isotherms with field observations in river water and sediments

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Sorption of alkylphenols on Ebro River sediments: Comparing isotherms with field observations in river water and sediments

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Laboratory sorption of nonylphenol compared to field concentrations showed good agreements.

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ABSTRACT

This study reports sorption isotherms of the endocrine disruptors nonylphenol (NP) and octylphenol (OP) in three sediment samples from the Ebro River basin (NE Spain), with organic carbon fractions (f_{OC}) ranging from 0.0035 to 0.082 $g_{OC} g^{-1}$. All isotherms were fitted to the Freundlich model with slightly nonlinear exponents ranging from 0.80 to 0.94. The solubility of the compounds as well as the organic carbon (OC) content had the strongest influences on the sorption behavior of these compounds. Comparison of the laboratory-spiked samples with the native contamination of NP of 45 water and concurrent sediment samples resulted in reasonable matches between both data sets, even though the lowest concentrations in the field were not completely reached in laboratory tests. This good agreement indicates that sorption laboratory data can be extrapolated to environmental levels and therefore the distribution of nonylphenol between sediments and water can be predicted with a precision of one order of magnitude. Furthermore, laboratory experiments with simultaneous loading of NP and OP revealed negligible competition for sorption sites at low concentrations.

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1. Introduction

Alkylphenol polyethoxylates are non-ionic surfactants used in a large variety of industrial and domestic applications (i.e. pesticide formulations and plastic additives) (Maguire, 1999; Hou et al., 2006) that can degrade to alkylphenols (APs). The environmental occurrence of APs such as nonylphenol (NP) and octylphenol (OP) has been investigated since the late 1970s (Sheldon and Hites, 1978; During et al., 2002) and their pervasive use, persistency and accumulation properties have led to a widespread distribution in various matrices (Dachs et al., 1999; Petrovic et al., 2002; Vazquez-Duhalt et al., 2006; Correa-Reyes et al., 2007). NP is present in the environment as a mixture of various 4-nonylphenol isomers (Isobe et al., 2001) whereas OP is found dominantly in the form of 4-*tert*-octylphenol. In the early 1990s, these compounds were shown to cause estrogenic activities (Moeder et al., 2006).

Most commonly APs reach the environment through the discharge of municipal and industrial wastewater treatment plants (WWTP) (United States Environmental Protection Agency, Office of Water, 2005). In most receiving aqueous systems this leads to a net accumulation, particularly in sediments (Petrovic et al., 2002). For instance, data from 2003 reported NP and OP in Ebro River sediments (Spain) at levels between 0.03 and 2.33 $mg kg^{-1}$ (dry weight) (Petrovic et al., 2002). This survey led to a more detailed monitoring campaign between 2004 and 2006 (unpublished data), during which NP and OP were detected in various sampling points along the whole Ebro River and some of its tributaries. In these surveys, NP reached concentrations of 0.025 $mg L^{-1}$ in water and 6 $mg kg^{-1}$ in sediment (dry weight). Moreover, OP was also identified at usually ~ 10 times lower concentrations than NP.

The above field monitoring data of the Ebro offer an ideal background to further investigate the environmental fate of NP and OP and helped to elucidate their sorption characteristics in sediments that can be transferred to other river basins. This study is timely, because sorption of APs has not been well investigated in sediments. In addition laboratory sorption data obtained under well-controlled boundary conditions have to our knowledge never been linked with field data from monitoring campaigns.

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Sorption—and thus the fate of APs—depends on several environmental parameters such as organic carbon (OC) content. Flow dynamics of the water may also control equilibrium conditions, and thus sorption kinetics. Considering a mobile system, pore water plays an important role, as sorption equilibrium is more easily achieved between it and the sediment matrix (Kraaij et al., 2003). With most of these factors being variable, the extrapolation of laboratory experiments to field conditions remains challenging. In addition, sorption experiments are often conducted at concentration levels that are orders of magnitudes higher than those occurring in the environment and thus the extrapolation of sorption isotherm data to field concentrations produce a source of uncertainty in risk assessment. This is due to the possible different sorption behavior of a compound at high and low concentrations. When solution concentration increases, nonlinearity should be expected (Weber et al., 1992) as it occurs because the affinity for solute decreases progressively with increasing solute concentration sites become filled (Xing et al., 1996). Sorption capacity of the various constituents of the organic matter also needs to be taken into account. For instance, black carbon is considered to have 10–1000 times more sorption strength than other forms of OC (Cornelissen and Gustafsson, 2006) and therefore is believed to be responsible for a large part of the sorption of some hydrophobic organic compounds in soils and sediments (Gustafsson et al., 1997; Accardi-Dey and Gschwend, 2002). Furthermore, competitive sorption with co-occurring contaminants may also affect sorptive behavior, leading to over- or under-estimation of the sediment capacity to retain APs (Pignatello, 1998), due to the fact that competition is the result of overlap in the set of sites that can be occupied by non-identical solutes (Xing et al., 1996).

The primary objective of this study was therefore to investigate the equilibrium sorption behavior of NP and OP in sediments from the Ebro River. The role of organic carbon content on sorption of NP was also considered and samples that represented the range of organic carbon concentrations in Ebro sediments were chosen. With this, equilibrium constants (K_{OC} values) derived from these laboratory experiments were compared with those from field data. In our study we extended sorption isotherms towards low concentration ranges that reach environmentally occurring maximum loadings. Furthermore, as OP and NP occur mostly together in the environment, the effect of simultaneous and potentially competitive sorption of these two compounds was investigated in this study.

2. Material and methods

2.1. Sorbents and chemicals

Sediments were sampled along the Ebro River Basin (NE Spain) in October 2006 (third sampling campaign). Sediments were collected using a Van Veen drag from the middle of the river, in order to obtain a representative sample. All sediments were characterized for their OC content and a suite of organic pollutants. Out of the 22 sediments sampled, three were selected for sorption studies: (i) from the Ebro Spring in Miranda de Ebro (R0), (ii) from the Araquil, a tributary of the Ebro (T8), and (iii) from the delta area (R20). The location of the three selected sampling sites is presented in figure S1 in supplementary information. These three selected samples took into account maximal differences in APs concentration and OC content (table S1 in supplementary information). The OC content of these samples was analyzed using the modified Pregl and Dumas method (dynamic flash combustion) using helium as the carrier gas. Table S1 in supplementary information also shows the OC of these samples, which were lowest in the delta sample (R20) and highest in the sample from the tributary (T8). Note that all three selected sediments contained relatively large amounts of native NP and OP. The sediments were freeze-dried at 10^{-2} mbar and subsequently pulverized for 45 min in a zirconium oxide planet ball mill (Planetmill Laborette 05.102, Fritsch). As a result, the grain size of at least 80% of the pulverized materials was <0.063 mm in diameter. This allowed sorption experiments to reach equilibrium within 1 week (Karapanagioti et al., 2000).

NP technical mixture (94% purity) was purchased from Riedel de Haën (Seelze, Germany), while 4-*tert*-octylphenol (98.5% purity) and 4-*n*-nonylphenol- d_8 (98% purity) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Chemical properties of NP and OP are presented in table S2 in supplementary information. NP

and OP were diluted in methanol. Methanol and cyclohexane at GC grade were purchased from Merck (Darmstadt, Germany).

2.2. Batch sorption experiments

The complete study consisted of five sorption experiments with NP or OP as single compounds and a sixth sorption experiment that combined NP and OP. For the sediment from the spring area of the Ebro (R0), the NP experiment was extended to lower concentrations to approach real field conditions. This sediment was also used to perform the OP sorption experiment and the NP and OP combined experiment.

All equilibrium batch experiments were conducted in triplicates in 20-ml glass vials with aluminum caps, except for the low concentration experiment with R0 sediment that was performed using 100-ml vials. Between 0.015 and 1 g of sorbent were weighed into the vials, which were filled with degassed milli-Q water with 200 mg L^{-1} NaN_3 (biodegradation inhibitor). Solid-to-water ratios ranged from 1:1300 to 1:115 and were adjusted depending on the expected sample sorption capacity. After 20–24 h pre-wetting time, NP or OP was added ranging from 0.3 to $58.5 \mu\text{g}$ and from 0.4 to $125.7 \mu\text{g}$, respectively in order to cover at least 4 orders of magnitude in concentrations. The amount of methanol added to the batches was kept $<0.2\%$ of the liquid volume in order to avoid co-solvent effects. The competitive sorption experiment was conducted following the same procedure with simultaneous addition of NP and OP at the same initial aqueous concentrations, ranging from 0.05 to 6.7 mg L^{-1} . Both compounds were added via a mixture stock solution containing these two compounds. In this case the solid-to-water ratio was 1:40.

Vials were shaken on a horizontal plate shaker at 150 rpm for 7 days at a constant temperature of 20°C in the dark. After centrifugation at 2500 rpm for 30 min (Metafuge 1.0R, Heraeus Sepatech), the solute was extracted from an aliquot of the supernatant with cyclohexane containing 4-*n*-nonylphenol- d_8 as internal standard. Blanks and controls were prepared at the same time under the same conditions. Blanks were set up using the same solid-to-water ratios as the samples but without adding NP or OP. Controls were prepared without sediment and at increasing concentration of the target compounds.

All extracts were analyzed by a gas chromatograph (GC) (Hewlett Packard 5890 series II) coupled to a quadrupole mass spectrometer (MS) (Hewlett Packard 5972) operating in the selected ion monitoring mode ($m/z = 149, 135, 121$ and 107 for NP and $m/z = 135, 107$ and 206 for OP). Target compounds were quantified using internal standard quantification and considering all chromatographic peaks for NP isomers as a whole. The NP and OP concentrations in the sediment were calculated by a mass balance, setting as initial water concentrations the ones found in the control vials. The final sediment concentration was corrected by adding the background contamination of the samples. Dissolved organic carbon (DOC) was analyzed to evaluate a potential solubilization effect of the compounds following Wang et al. (2007). However, no significant differences were found between the original data and the DOC-corrected values and the following results are presented without this correction. More information about the DOC effect in the supernatant is given in supplementary information.

Information regarding quality assurance and quality control is available in figure S2 in supplementary information.

3. Results and discussion

3.1. Sorption isotherms

The Freundlich parameters were calculated by regression analyses using the equation $C_S = K_F \cdot C_W^{1/n}$, where C_S is the concentration of a chemical adsorbed in the solid phase (mg kg^{-1}); C_W is the equilibrium solution concentration (mg L^{-1}); K_F is the Freundlich coefficient ($(\text{mg kg}^{-1})/(\text{mg L}^{-1})^{1/n}$) and $1/n$ the Freundlich exponent, and are summarized in Table 1. This approach fitted the experimental data well and produced squared correlation coefficients (R^2) higher than 0.97. The isotherms were found to be slightly nonlinear, with the $1/n$ exponent ranging from 0.80 to 0.94. The least linear isotherm belongs to the sediment with lowest OC content ($0.0035 \text{ g}_{OC} \text{ g}^{-1}$).

Fig. 1a shows the four isotherms with NP as the target compound in the three different sediments from the Ebro River Basin. $\log K_F$ increases with f_{OC} (cf. Table 1), indicating stronger sorption in the sediment with increasing OC content. The same figure shows the isotherms without background concentration corrections for each sediment. They indicate that without correction, the low concentration points deflect from the isotherm. Therefore, sediment field concentrations also had to be considered in addition to sorbed concentration from laboratory experiments.

Table 1
Freundlich parameters and organic carbon-normalized distribution coefficients (K_{OC}) of NP and OP obtained from the sorption experiments

Isotherm	Sediment	Compound	Freundlich isotherm parameters			$\log K_{OC}^a$
			$\log K_F$	$1/n$	R^2	
R20		NP	1.74 ± 0.03	0.80 ± 0.03	0.986	4.13–4.65
R0		NP low	2.93 ± 0.07	0.88 ± 0.07	0.988	4.37–4.54
R0		NP high	2.94 ± 0.03	0.91 ± 0.03	0.989	4.16–4.39
R0 ^b		NP	2.93 ± 0.03	0.89 ± 0.01	0.995	4.14–4.53
T8		NP	3.44 ± 0.02	0.93 ± 0.01	0.998	4.52–4.69
R0		OP	2.50 ± 0.05	0.82 ± 0.04	0.975	3.60–4.19
R0		OP ^c	2.41 ± 0.05	0.94 ± 0.03	0.979	3.63–3.79
R0		NP ^c	2.91 ± 0.09	0.86 ± 0.04	0.966	4.23–4.59

^a Parameter calculated at highest and lowest concentration of each isotherm.

^b Combined NP isotherm on R0 sediment from high and low isotherms.

^c Competition experiment.

After this correction, the low concentration sorption isotherm on sediment R0 is lined up with the high concentration one as the difference in the obtained Freundlich parameters is 0.01 units for K_F and 0.03 units for $1/n$. This can be an indication that the majority of preloaded NP was exchangeable and behave equivalently to added NP. The Freundlich parameters are the same for both low and high concentration isotherms (Table 1). This confirms the same sorption behavior for NP over the entire range of concentrations tested. From now on, NP isotherm on R0 sediment considers both low and high concentration data points and is presented as a single isotherm.

Fig. 1b shows the three isotherms normalized to the f_{OC} . They overlap in the same area of the plot, indicating a comparable composition of the organic matter in the three samples, particularly concerning black carbon and other strong sorption capacity materials. This also indicates the predominant role of the OC content in the sorption process. $\log K_{OC}$ values for the different isotherms were calculated at varying concentrations based on equation $K_{OC} = K_d \cdot f_{OC}^{-1}$ where $K_d = C_s \cdot C_w^{-1}$ and f_{OC} is the fraction of OC present in the sample (Schwarzenbach et al., 2003; Ying et al., 2003; Hou et al., 2006), and are summarized in Table 1. The resulting $\log K_{OC}$ values for NP fall in a narrow range, varying from 4.13 to 4.69. The observed weak sorption nonlinearities lead to differences of up to 0.5 in $\log K_{OC}$ between the highest and lowest concentrations. This outlines the variability in the $\log K_{OC}$ values, as also found in other studies with organic chemicals such as carbon tetrachloride, 1,2-dichlorobenzene, benzene, 1,1,1-trichloroethane and naphthalene as target compounds (Larsen et al., 1992; Kile et al., 1995). $\log K_{OC}$ values for OP (3.60–4.19) are slightly lower than for NP. $\log K_{OC}$ values obtained in the competitive experiment are in the same range of the ones from the single isotherms for both compounds.

Fig. 2a shows OP and NP isotherms for the R0 sediment, as well as the solubility-normalized isotherms for both compounds

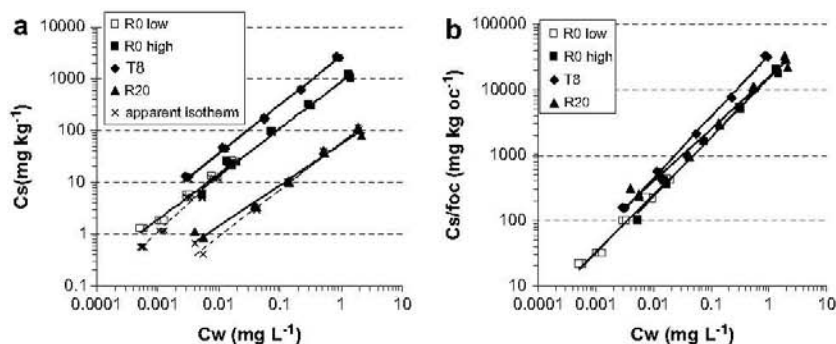


Fig. 1. NP isotherms for the three considered sediments: (a) sorption data, (b) f_{OC} normalized sorption data.

(Fig. 2b). These isotherms differ by 0.07 units in the $1/n$, which means 8.5% of difference. This leads to comparable slopes of the isotherms when plotted on a logarithmic scale. In addition, Fig. 2b shows that normalization of the aqueous concentrations to the solubility of each compound leads to an overlapping of both isotherms in the figure. This indicates the same loadings at the same activity (C_w/S) of OP and NP. The lower position of OP isotherm in Fig. 2a indicates that sorption of OP is weaker than for NP.

3.2. Competitive sorption of NP and OP

Fig. 3 shows the single isotherms for both compounds (black symbols) as taken from Fig. 2a together with the results from the simultaneous NP and OP experiment (gray symbols). The results obtained for NP indicate corresponding behavior under both conditions and only show a slightly lower $\log K_F$ and $1/n$ for the competition isotherm (see Table 1). Both coefficients also lie within the experimental error. However, for the OP isotherm obtained from the competition experiment, we found a shift of the sorption isotherm towards lower C_s values and a steeper slope than single OP isotherm. This indicates weaker sorption and an increase of the linearity from $1/n = 0.82 \pm 0.04$ to $1/n = 0.94 \pm 0.03$ when OP is combined with NP. The increase of linearity under competition conditions has been documented in other studies (Xing et al., 1996; Pignatello, 1998). Nonetheless, the shifts of the combined isotherms for OP are of the same order of magnitude of the experimental error for K_F and slightly higher for $1/n$. The experiment shows that in the investigated conditions there is no competition for NP while for OP there is a reduced influence in the sorption process caused by the competition of NP. Pignatello (1998) concludes that competitive studies appear to show that structurally similar molecules compete more strongly. Although OP and NP have similar structures, the branching of each of the compounds is different. In addition NP is an isomeric compound while OP is found only in the form of 4-ter-OP. This can lead to a better adaptation of each of the NP isomers to the multiple types of sorption sites that reduces the effect of a competitor. Furthermore, stronger competition is expected when the competitor concentration increases (Pignatello, 1998; Sander and Pignatello, 2005). In our case competition was tested at a given concentration and consequently only one degree of competition has been observed.

3.3. Comparison of sorption isotherms with in-situ measurements in the field

In most cases the isotherms were measured in convenient concentrations allowing high accuracy in the analytical measurements. However, for sediment R0 an isotherm with two orders of

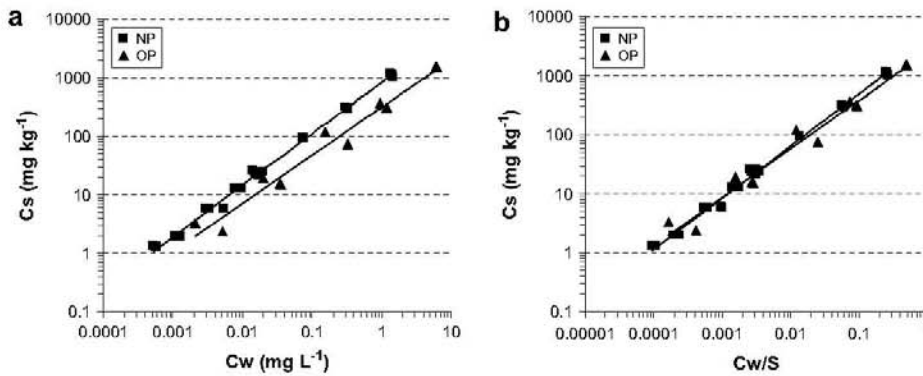


Fig. 2. NP and OP isotherms for R0 sediment: (a) sorption data, (b) solubility normalized data.

magnitude lower concentration was achieved and it was able to simulate the highest environmental levels. For prediction of further lower concentrations in the field extensive extrapolation is necessary, leading to some uncertainty in the interpretation of results. Fig. 4 compares the isotherms determined for NP in the three sediments considered and the NP concentrations in river water and sediment from 45 Ebro samples collected between 2004 and 2006 (see table S4 in supplementary information). Fig. 4 shows that the experimental sorption isotherms are in reasonable agreement with the concentrations observed in the field (Fig. 4a). None of the field samples fall outside the area limited by the isotherms, so the relationship between the water and sediment concentration obtained in the field is consistent with the NP isotherms performed in the laboratory. This fact mitigates the uncertainty from the extrapolation to lower concentrations and shows that, taking the Ebro Basin as a whole, the correlation obtained between the field and experimental data from the laboratory provides a good means of comparison.

As the differences on the f_{OC} explain the variations of the isotherms (Fig. 1b), both the experimental isotherms from the laboratory and the field samples were normalized to their OC content and plotted in Fig. 4b. In this figure one representative isotherm is generated using the OC-normalized data from the three original isotherms and the field samples are divided into three categories depending on the OC content:

- (1) Samples with more than $0.06 \text{ g}_{OC} \text{ g}^{-1}$ (■)
- (2) Samples with less than $0.01 \text{ g}_{OC} \text{ g}^{-1}$ (●)
- (3) The remainder of the samples, with f_{OC} ranging between $0.01 \text{ g}_{OC} \text{ g}^{-1}$ and $0.06 \text{ g}_{OC} \text{ g}^{-1}$ (*)

Fig. 4b shows that half of the field samples are within the 95% prediction intervals of the combined isotherm. NP at these sites thus may be in near-equilibrium between sediment and overlying river water. On the other hand, some field samples show substantially higher or lower concentrations of NP in the sediments than expected from the laboratory experiments. This is probably because of non-equilibrium conditions in terms of NP partitioning at these sites. Owing to the movement of the water mass in the river, it is conceivable that NP in water at a specific point in the river is not in equilibrium with the sediment samples. The present study suggests the possibility that there are some local net fluxes of NP between the sediment and overlying water in the field. That is, the sediment serves as a source of NP to river water at some sites, while the sediment is a sink at the sites where the aqueous concentration lies below the isotherm. Note that samples with low f_{OC} , i.e., less than $0.01 \text{ g}_{OC} \text{ g}^{-1}$, tend to show higher sediment concentrations than expected. Two possibilities are considered to explain the disagreement between the isotherms and the field concentrations that do not match the isotherms. First, this could be due to differences in properties of the OC. Some forms of OC (e.g. black carbon (Yang et al., 2008)) are known to have higher sorption strength, the influence of which may be more pronounced on samples with low f_{OC} . If this is the case, our combined isotherm does not represent the equilibrium conditions of these samples and the sediments can retain more NP than expected. We would also expect much better agreements between isotherms and field concentrations if sediment pore water instead of main river water would be sampled. Recent studies show that pore water concentrations are higher compared with overlying water (Booij et al., 2003; Cornelissen et al., 2008). This means that overlying river water sampling can lead to under-estimation of liquid phase concentrations.

3.4. Comparison of K_{OC} from sorption isotherms with literature data

The experimental $\log K_{OC}$ values obtained in this study are compared with other reported results from different sources and presented in Table 2. It includes:

- (a) Experimentally derived K_{OC} values from laboratory studies
- (b) In-situ K_{OC} values based on monitoring data from field studies
- (c) K_{OC} values obtained from empirical correlations with K_{OW} for these species

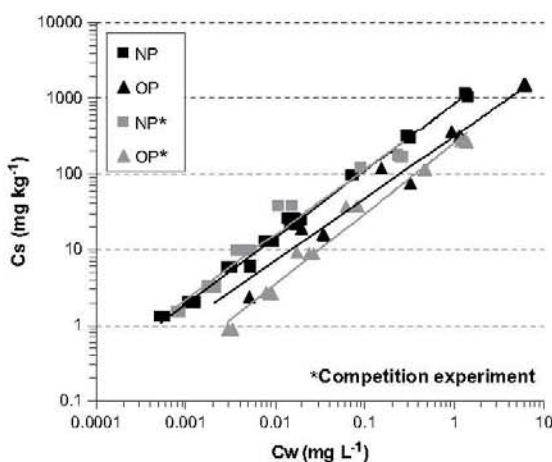


Fig. 3. OP and NP isotherms for R0 sediment obtained in single experiments (black) and in competitive sorption isotherms (gray).

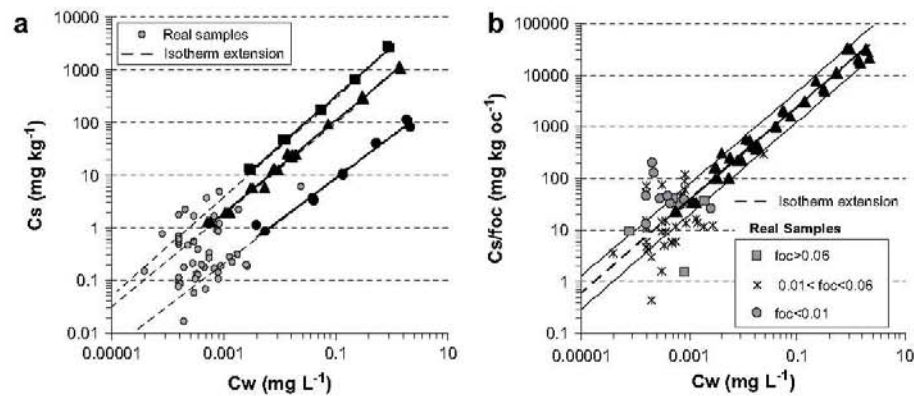


Fig 4. Field samples water and sediment concentrations in comparison with the NP sorption isotherms determined in the three sediments considered: (a) sorption isotherms and field samples, (b) f_{OC} normalized sorption isotherms and f_{OC} normalized field samples. In (b), a Freundlich isotherm derived using all isotherm data for three sediments is drawn with 95% prediction intervals.

Table 2

Data compilation of K_{OC} -coefficients derived from in-situ measurements, laboratory studies, and empirical correlations

Source	References	NP	OP
Experimental $\log K_{OC}$ values from laboratory studies			
	Ying et al. (2003)	4.59	–
	Hou et al. (2006)	5.12	–
	Johnson et al. (1998)	–	3.54–4.27
	Zhou (2006)	–	4.63
In-situ K_{OC} values based on monitoring field studies			
	Sediments	Ferguson et al. (2001) Sekela et al. (1999)	5.39 4.7–5.6
	Soils	Isobe et al. (2001) During et al. (2002) Höllrigl-Rosta et al. (2003)	5.22 3.97 3.96
Log K_{OC} values based on empirical correlations			
	Karickhoff et al. (1979) ^a	4.27	3.91
	Karickhoff (1981) ^b	4.08	3.73
	Xia (1998) ^c	4.23	3.88
	Xia (1998) ^d	4.03	3.65
Log K_{OC} (batch experiments)			
	This study	4.13–4.69	3.60–4.19

^a $\log K_{OC} = 11 \log K_{OW} - 0.21$.

^b $\log K_{OC} = 0.989 \log K_{OW} - 0.346$.

^c $\log K_{OC} = 0.97 \log K_{OW} - 0.12$.

^d $\log K_{OC} = 1.06 \log K_{OW} - 0.72$.

The $\log K_{OC}$ values obtained in the study—between 4.13 and 4.69 for NP and between 3.60 and 4.19 for OP—are in good agreement with the ones obtained in other sorption experiments conducted with sediments. Generally, experimental $\log K_{OC}$ values are lower than the ones obtained from monitoring data on sediments and higher than the ones from monitoring data on soils, thus confirming stronger sorption behavior of APs in sediments than in soils.

Among others (Chiou et al., 1984; Curtis et al., 1986; Sabljic, 1987; Schwarzenbach et al., 2003), Karickhoff et al. (1979), Karickhoff (1981) and Xia (1998) provided equations to calculate $\log K_{OC}$ based on the octanol/water partition coefficient. $\log K_{OC}$ values calculated on the basis of these correlation equations are of the same order as the experimental values for both compounds found in this study (cf. Table 2). Note, however, that these empirical correlations were obtained using mainly PAHs and PCBs that show higher K_{OC} s.

4. Conclusions

Overall, our results indicate a high linearity of alkylphenol sorption in sediments. Variations in the data sets are primarily related to the solubilities of the compounds and to the OC content

of the sorbents, as could be shown by much reduced variability after normalization to these factors. Competitive sorption between OP and NP was tested but was shown to cause only a reduced effect for OP on concurrent environmental behavior. We also found consistency with other data on sorption from both literature and empirical relationships. Furthermore, sorption coefficients obtained in spiked laboratory experiments agreed well with the distribution of native NP between water and sediment at many field sites. This indicates that the sorption data obtained with batch experiments at high concentrations can with caution be extrapolated to environmental levels. In summary, the distribution of nonylphenol between sediments and water can be predicted with a precision of one order of magnitude based on existing empirical correlations with K_{OW} . Comparison of field data consisting of river water and sediment concentrations indicates that Ebro River water is not always in equilibrium with the sediments, this effect could be minimized considering pore water instead of overlying water. Contaminant fluxes can occur from the water to the sediments and vice versa depending on the location.

The accompanying supplementary information includes details on the study area, the DOC effect, the quality control section and

tables S1–S4, containing properties of sorbents (sediments) analyzed, the properties of the sorbates (analytes) and the concentration of NP in Ebro samples.

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Appendix A. Supplementary material

Supplementary information for this manuscript can be downloaded at doi: 10.1016/j.envpol.2008.08.007.

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Supporting Information for

Sorption of alkylphenols on Ebro River sediments: Comparing isotherms with field observations in river water and sediments*Study Area*

The Ebro River Basin (NE Spain) (Figure S1) drains an area of approximately 85,000 km². It discharges into Mediterranean Sea and forms a delta of more than 300 km². The whole basin has more than 2,700,000 inhabitants. One-third of the population lives in small villages with less than 5,000 inhabitants and only 5 cities, next to the Ebro River or its tributaries, concentrate approximately 45% of the populations of the whole basin. The region is mostly agricultural and

counts among the most important irrigated areas in Spain. It covers the areas of La Rioja (wine production), Lleida (fruit trees and corn production) and the Ebro Delta (rice production) (Petrovic et al., 2002). The Ebro Basin is also dominated by industrial activities that concentrate around the cities of Zaragoza, Vitoria, Pamplona, Logroño, Monzón, Tortosa, Flix and Lleida (Figure S1).

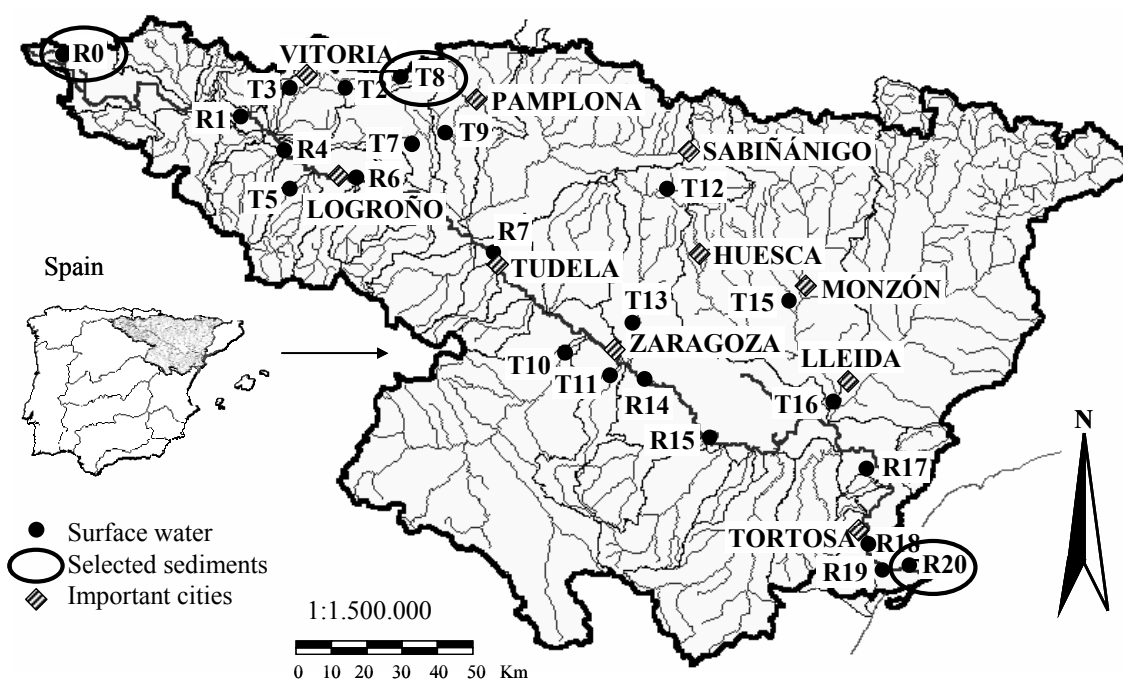


Fig S1. Location of sampling sites and important cities in the Ebro River Basin.

Table S1
Location and properties of sorbents

Sediment	UTM coordinates		Location	f_{oc} (goc g ⁻¹)	Field concentration ^a	
	X	Y			NP (mg kg ⁻¹)	OP (mg kg ⁻¹)
R0	405,987	4,761,433	Spring area, remote	0.058	0.68	0.002
T8	570,609	4,749,543	Tributary, industrial	0.082	0.74	0.028
R20	306,867	4,509,550	Delta area, agricultural	0.004	0.45	0.002

^a Measured concentration of alkylphenols on the sediments used as sorbents

Table S2
Properties of Sorbates

Compound	CAS	Molecular weight (g mol ⁻¹)	Solubility (mg L ⁻¹) (Ahel and Giger, 1993a)	Log K _{ow} (Ahel and Giger, 1993b)
Nonylphenol technical mixture (NP)	84852-15-3	220.35	5.43	4.48
4-tert-Octylphenol (OP)	140-66-9	206.33	12.6	4.12

DOC effect

For nonpolar organic compounds, the solubility enhancement due to DOC present in the aqueous solution can be significant (Wang et al., 2007). In order to account for this, potential impact on the aqueous concentration was estimated with the following relationship:

$$C_w = C_w^* \cdot (1 + f_{\text{DOC}} \cdot K_{\text{DOC}})^{-1} \quad (1)$$

where C_w^* is the measured apparent aqueous concentration (mg L⁻¹); f_{DOC} is the fraction of dissolved organic carbon (kg L⁻¹) and K_{DOC} is the partitioning coefficient between water and DOC. K_{DOC} values were

estimated with the following relationship (Schwarzenbach et al., 2003):

$$\log K_{\text{DOC}} = 0.91 \cdot \log K_{\text{OW}} + 0.16 \quad (2)$$

To date, the majority of studies on the sorption of organic compounds to DOC have been conducted with PAHs. Nevertheless, due to the lack of more sophisticated approaches, in practice simple relations as equation 2 are presently the only means to make a reasonable prediction of K_{DOC} . The results obtained using this approach are summarized in Table S3

Table S3
DOC and % of NP and OP sorbed to DOC obtained from the sorption experiments

Isotherm		DOC effect		
Sediment	Compound	K_{DOC}	DOC	% sorbed to DOC
R20	NP		2.3	3.82
T8	NP		5.5	8.67
R0	NP low	17,250	1.3	2.23
R0	NP high		1.6	2.66
R0	NP*		1.5	2.59
R0	OP*	8,113	1.5	1.24
R0	OP		1.7	1.35

* Competition experiment

The mass potentially associated with DOC varies between 1.24 and 8.67% depending on the compound and the sediment used to perform the isotherm. These values, all fewer than 10% of the total concentration of

the compound in the supernatant, indicate that the DOC effect is minimum and the consideration of this parameter in the sorption calculations would not considerable change the results obtained.

Quality Control

No target analytes (i.e. NP and OP) were detected in the blanks. On the other hand, loss in the controls was found to increase when the concentration decreased. Less than 10% system loss was found in the high concentration controls while up to 50% of the target analytes were lost in some of the low concentration controls. For our experiments most system loss was estimated on the order of 10% or less as sorption to sediments further reduces the system loss when compared to reference vials. The concentrations

of NP and OP in the controls were taken as initial water concentration, assuming the same system loss in the samples.

The largest part of the system loss can be caused by biodegradation and sorption to the caps. Previous to all sorption experiments, conditions that might affect the sorption process were tested using NP at high concentration on R0 sediment. Firstly, the isotherm was realized using PTFE caps and pure degassed water, without the addition of any biodegradation inhibitor.

Subsequently, two concentration levels were repeated using aluminum caps and adding NaN_3 (biodegradation inhibitor) at 200 mg L^{-1} into the water solution. The results obtained from these two different approaches were plotted into the same graph. In the first place, the complete isotherm realized with PTFE caps and no poisoning was represented, and once the Freundlich isotherm was adjusted, the repetition of the two different levels were added to the graph. This led to a very good fitting with the previous isotherm (Figure S2). Furthermore, the losses in the controls were significantly lower using aluminum caps and after poisoning the water. This indicates adsorption of the target compounds on the PTFE caps as the most dominant mechanism for system loss. All experiments were therefore continued with aluminum caps and under poisoned conditions.

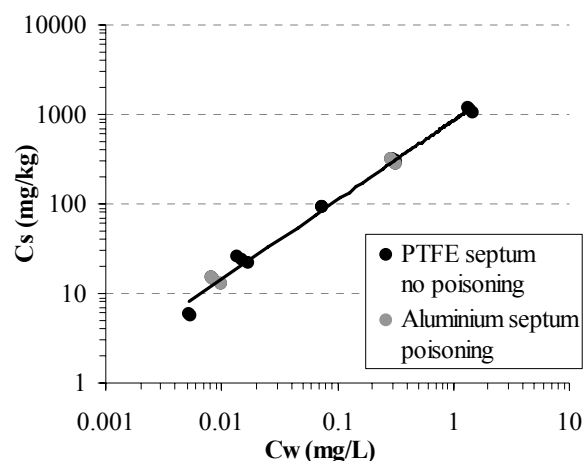


Fig S2. Differences between the isotherms obtained with the two different conditions tested

Table S4
Monitoring data of NP in river sediment and water among the Ebro basin

Sampling site	Sampling campaign	Water concentration ($10^{-3} \text{ mg L}^{-1}$)	Sediment concentration ($\text{mg kg}^{-1}\text{-dw}$)	f_{oc} ($\text{g}_{oc} \text{ g}^{-1}$)
R0		0.16	0.09	0.020
R1		0.16	0.07	0.006
T2		0.83	0.10	0.067
T3		1.92	2.17	0.060
R4		2.77	0.18	0.015
T5		0.16	0.08	0.002
R6		1.42	0.22	0.016
R7		1.30	0.28	0.017
T7		2.50	0.20	0.008
T8		0.82	0.83	0.014
T9	October 2004	0.88	0.18	0.013
T10		0.68	0.16	0.005
T11		24.29	6.00	0.020
T12		0.31	0.11	0.011
T13		0.81	0.14	0.004
R14		1.81	0.30	0.026
T15		0.56	0.25	0.022
T16		0.45	0.17	0.005
R17		0.36	0.13	0.014
R19		0.29	0.21	0.005
R20		0.41	0.20	0.004
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R0		0.17	0.08	0.020
R1		0.33	0.13	0.028
R4		0.20	0.17	0.057
R6		0.16	0.11	0.019
T7		0.68	1.62	0.035
T8		0.20	0.02	0.039
T9	October 2005	0.16	1.80	0.026
T11		0.83	4.90	0.042
R14		0.30	0.54	0.038
T15		0.48	0.07	0.012
T16		0.55	0.33	0.057
R20		0.78	0.88	0.026
<hr/>				
R0		0.16	0.68	0.058
T3		0.51	3.66	0.088
T5		0.21	2.14	0.011
T8		0.08	0.74	0.082
T10		0.30	1.70	0.023
T11		0.84	1.17	0.013
T13	October 2006	0.16	0.49	0.046
T15		0.16	0.61	0.011
R15		0.36	0.38	0.024
T16		0.04	0.15	0.041
R19		0.16	0.52	0.035
R20		0.23	0.45	0.004

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5.4.- Discussió addicional als articles

L'experiment de degradació de NP, OP i diazinon tenia per objectiu avaluar les cinètiques de degradació dels diferents compostos sota quatre condicions diferents (llum i foscor en combinació amb condicions aeròbiques i anaeròbiques), totes elles intentant reproduir les condicions ambientals. Amb aquesta finalitat les ampolles on es va portar a terme l'experiment es van emplaçar al terrat de l'edifici de l'IDAEA-CSIC amb incidència directa de la llum solar, tal i com es pot apreciar a la [Figura 5.1](#).



Figura 5.1: Disposició de les ampolles per a l'experiment de degradació a condicions ambientals a l'exterior dels laboratoris

Es van utilitzar ampolles de vidre incolor i ambre per tal de simular diferents condicions de llum i poder avaluar així l'efecte de la fotodegradació. La [Figura 5.2](#) mostra l'espectre de la radiació solar en entrar a l'atmosfera i al nivell del mar. Aproximadament la meitat de la llum solar que arriba a la Terra es troba en el rang del visible de l'espectre electromagnètic, mentre que l'altra meitat es troba a l'infraroig proper. Així mateix, una petita fracció forma part del rang de l'ultraviolat (IPCC, 2001). En principi com més energètica és una radiació, més susceptible és de produir fotodegradació, per tant la radiació ultraviolada i la visible són les que

poden donar lloc a aquest procés en l'experiment de degradació. Per tal de controlar aquests dos tipus de radiació es va mesurar la quantitat llum que traspassava cadascun dels vidres amb un radiòmetre PUV-2500 Ultraviolet Radiometer (Biospherical Instruments Inc., San Diego, USA), que mesurava la quantitat de radiació a 6 longituds d'ona de l'ultraviolat (305, 313, 320, 340, 380 i 395 nm) a més a més del rang del visible (400-700 nm).

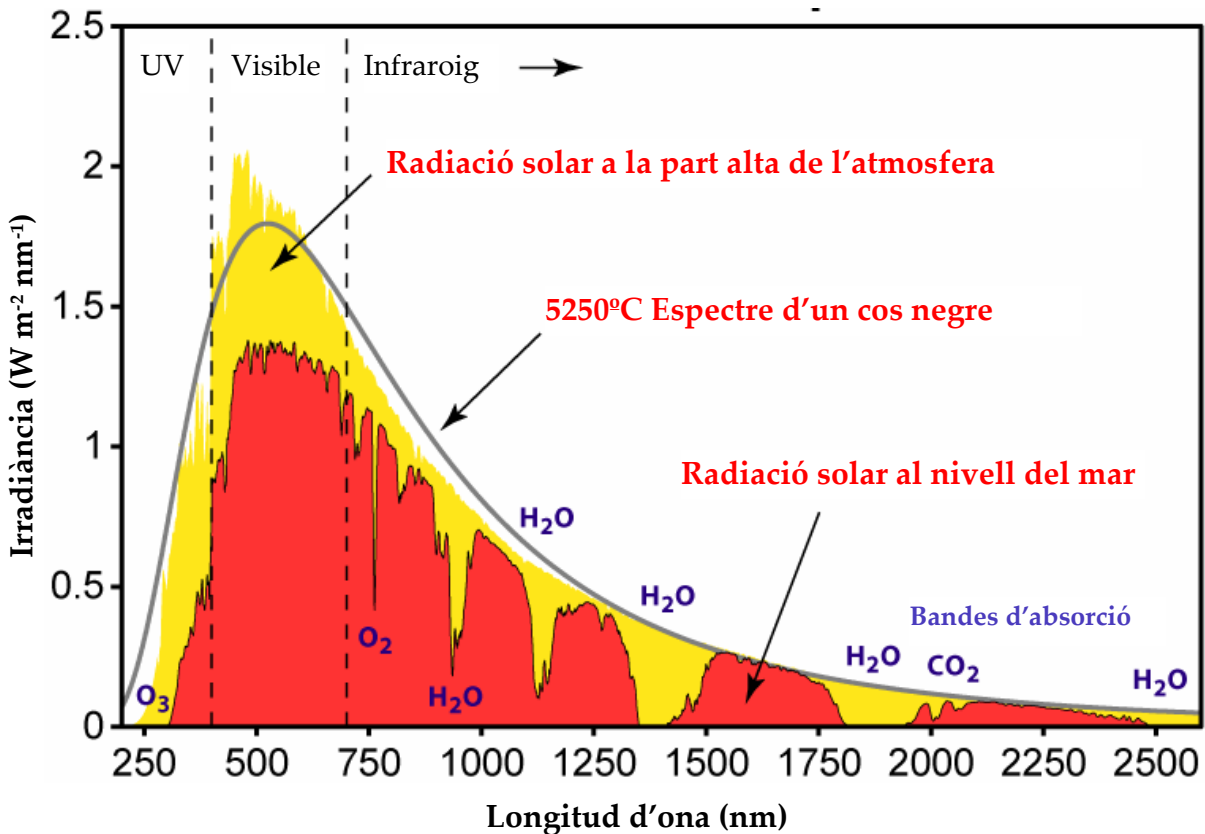


Figura 5.2: Espectre de radiació solar a l'atmosfera terrestre i al nivell del mar

A la [Figura 5.3](#) es mostren gràficament els resultats obtinguts, en primer lloc de la radiació solar directa i seguidament de l'atenuació obtinguda amb el vidre incolor i amb el vidre ambre. Es van realitzar mesures cada 0,2 segons durant aproximadament 1 minut per a cadascuna de les 3 situacions. Amb el vidre incolor es va observar molt poca atenuació per a les longituds d'ona de 395 nm, 380 nm i el rang del visible, mentre que les altres 4 longituds d'ona van presentar una disminució més elevada de la quantitat de radiació que traspassa el vidre. En canvi amb el vidre ambre l'atenuació va ser pràcticament total, per a totes les longituds d'ona, excepte per al rang del visible, on aquesta va ser una mica menor.

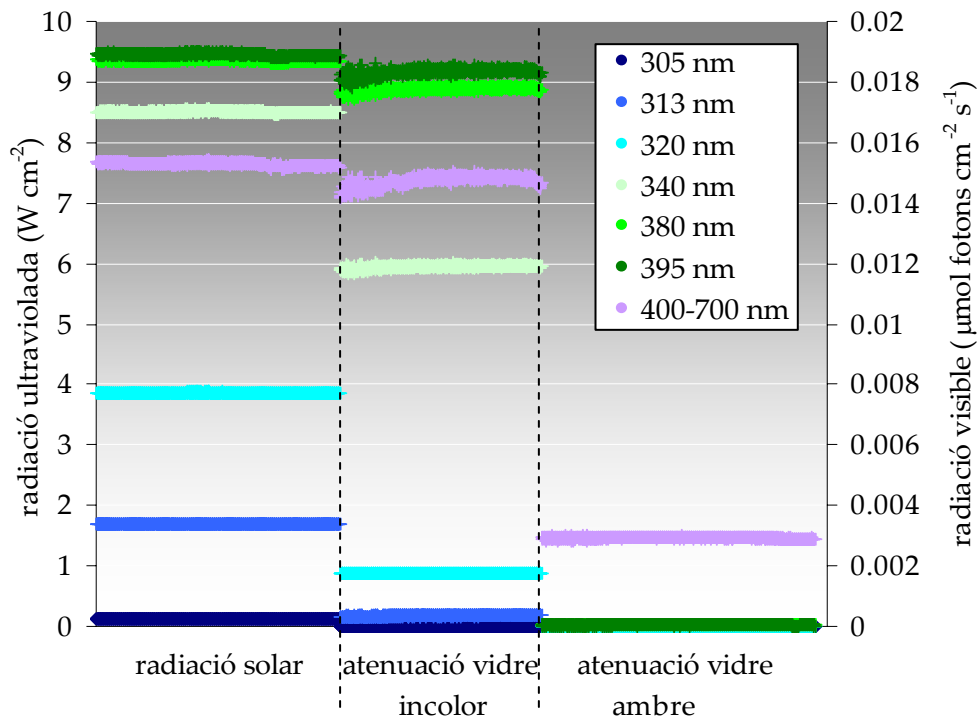


Figura 5.3: Espectres de radiació solar directa, l'atenuada pel vidre incolor i pel vidre ambre

Per tal de quantificar l'atenuació ocasionada pels dos tipus de vidre es van calcular els percentatges de radiació que traspassava el vidre prenent com a base la radiació solar mesurada directament. Els percentatges obtinguts es mostren a la [Taula 5.1](#). Per al vidre incolor hi va haver un augment de l'atenuació a mesura que disminuïa la longitud d'ona, de forma que per a la longitud d'ona de 305 nm el vidre només va deixar passar un 2,35% de la radiació. En canvi per a 340 nm va passar el 70% de la radiació mesurada i per a les altres longituds d'ona més llargues (380, 395 i 400-700) més del 95%, per tant podríem dir que l'atenuació en aquests casos va ser molt baixa. Per al vidre ambre es va perdre més d'un 80% de la radiació del visible i pràcticament la totalitat per a les altres 6 longituds d'ona. Amb aquestes dades podem concloure que el vidre ambre utilitzat pràcticament no va deixar passar la radiació solar per a les longituds d'ona mesurades i el vidre incolor deixa passar un percentatge elevat per a la major part d'elles. L'atenuació més important en el vidre incolor es va donar per a l'ultraviolat més llunyà, que com ja s'ha vist, arriba en una fracció molt petita a l'escorça terrestre. Per tant l'atenuació d'aquesta fracció de l'espectre va influir molt poc en el procés de degradació. Amb totes aquestes consideracions, la diferència pel que fa a radiació solar amb els dos vidres utilitzats va ser prou gran com per a afirmar que es van generar dues condicions de llum

diferents i per aquesta raó es poden atribuir a la fotodegradació els canvis en la degradació dels compostos utilitzant les dues condicions.

Taula 5.1: Percentatge de radiació solar que travessa els dos tipus de vidre utilitzats

Longitud d'ona	305	313	320	340	380	395	visible (400-700)
% radiació vidre incolor	2.35	10.18	22.86	69.88	94.95	96.94	96.31
% radiació vidre ambre	0	0.07	0.08	0.27	0.29	0.17	19.15

Els resultats obtinguts per a la degradació de NP i OP sota les quatre condicions esmentades es recullen a la Taula 5.2. Comparant les vides mitjanes ($T_{1/2}$) dels dos compostos per als quatre processos estudiats es va observar com en tots els casos la degradació obtinguda amb les ampolles incolores era més ràpida que la seva equivalent amb ampolla ambre, mentre que les condicions d'oxigenació tenien poca influència en la velocitat de la degradació. Conseqüentment, tant en el cas del NP com en el de l'OP, la fotodegradació va ser el procés majoritari per a la degradació d'aquests dos compostos. Això mateix es va observar amb els percentatges d'eliminació teòrica al cap dels 70 dies que va durar l'experiment, calculats a partir de l'equació de degradació. Aquests percentatges van ser més elevats en els casos en els que la degradació es va portar a terme en ampolles incolores. En el cas dels percentatges d'eliminació real, els valors van ser menors que per a l'eliminació teòrica però van seguir el mateix esquema. L'única excepció es va donar per al NP en condicions anaeròbiques i ampolla incolora, on l'eliminació es va equiparar amb l'obtinguda en les mateixes condicions d'oxigenació però amb ampolla ambre. Aquest fenomen indica que, tot i que la fotodegradació segueix sent el procés més important, la biodegradació aeròbica va tenir un major pes que l'anaeròbica

Pel que fa a la comparació entre la degradabilitat dels dos compostos, en tots els casos l'OP es va degradar més ràpidament que el NP, amb vides mitges entre 15,2 i 30,3 dies, mentre que per al NP aquestes van variar entre 28,3 i 44,7 dies, segons les condicions. Aquest fet va donar lloc a una major eliminació de l'OP després del període considerat, tant si es calcula l'eliminació real com la teòrica, arribant pràcticament a l'eliminació total en els casos en els que es va utilitzar l'ampolla incolora. Mentre que l'eliminació real del NP només va sobrepassar el 50% per a condicions aeròbiques i ampolla incolora.

Taula 5.2: Resultats obtinguts per a la degradació dels APs sota diferents condicions

	Condicions d'oxigenació	Ampolla	Equació de la degradació	t _{1/2} (dies)	r ²	Eliminació real (%)	Eliminació teòrica (%)
NP	Aeròbiques	Incolora	3,59e ^{-0,02t}	28,3	0,71	64	80
	Aeròbiques	Ambre	3,34e ^{-0,02t}	41,9	0,78	51	68
	Anaeròbiques	Incolora	2,93e ^{-0,02t}	30,2	0,88	47	81
	Anaeròbiques	Ambre	2,77e ^{-0,02t}	44,7	0,92	48	67
OP	Aeròbiques	Incolora	14,02e ^{-0,06t}	15,2	0,88	92	98
	Aeròbiques	Ambre	8,88e ^{-0,02t}	29,4	0,82	65	80
	Anaeròbiques	Incolora	9,90e ^{-0,05t}	17,0	0,94	91	97
	Anaeròbiques	Ambre	8,03e ^{-0,03t}	30,3	0,87	79	82

Pel que fa a la sorció, es va estudiar més profundament per al NP degut a que aquest és el més ubic dels dos APs estudiats. A part de les isoterms que es mostren a l'article 9, totes elles per a sediments provinents de la conca de l'Ebre, es van obtenir dues més en dos materials orgànics no contaminats amb APs, el lignit i un tipus de torba anomenada Pahokee. Ambdós materials tenen com a característica principal uns valors de COT molt per sobre dels mesurats en sediments, de 38,9 i 47,8% respectivament.

Portar a la pràctica la teoria dels processos de sorció és complicat, especialment perquè moltes de les variables que hi prenen part són desconegudes inicialment. Per això cal treballar amb el sistema de prova i error en el que es fa una estimació inicial de les variables per anar-les ajustant un cop es tenen els resultats. L'obtenció de dades experimentals adequades per a l'obtenció d'isoterms requereix treballar en unes condicions en que hi hagi una sorció significativa, mentre que a la fase aquosa hi resti una concentració que pugui ser quantificada amb seguretat amb la metodologia analítica que s'utilitza. Per això cal tenir ben seleccionats la massa de sediment, el volum de solució i la concentració inicial del compost. En base a la solubilitat i a la K_{ow} del compost i al COT del sorbent es va fer una estimació inicial de la K_F i del 1/n de la isoterma. Si l'estimació inicial era bona i els resultats s'ajustaven bé a una isoterma es podien calcular la K_F i el 1/n reals. Quan l'estimació inicial es desviava molt de l'experimental calia repetir la isoterma variant els paràmetres inicials segons el coneixement adquirit. Va ser per tant un procés lent en el que es podia donar el cas que una única isoterma s'hagués de repetir diverses vegades. Per al NP es va estudiar la sorció en 5 materials diferents (els 3

sediments de l'Ebre i els dos materials orgànics) i per a un d'ells, el sediment R0, es va voler estudiar el procés a concentracions més properes a les ambientals de forma que va caldre redimensionar l'experiment. A la [Taula 5.3](#) es mostren els paràmetres inicials i els resultats obtinguts per a cadascuna de les isoterms realitzades amb el NP com a sorbat.

En aquesta taula es pot veure com les condicions experimentals i l'estimació dels coeficients inicials per al sediment R0 i el T8 així com per a la torba van ser adequades com per a obtenir bons resultats en el primer intent. No va passar el mateix amb les altres isoterms, com per exemple per al sediment R0 a concentracions més baixes, per al que es van requerir tres isoterms en condicions diferents per a obtenir una bona correlació. L'obtenció de la isoterma del lignit va ser especialment complicada ja que donava lloc a una K_F per al NP inusualment elevada i presentava problemes analítics degut a la gran dispersió d'aquest material en la dissolució durant el procés d'extracció. Finalment només es va poder obtenir una isoterma tot i que amb certa dispersió en els triplicats.

Taula 5.3: Dades experimentals de la realització de totes les isoterms de sorció

	COT (%)	K_F	1/n	Volum (mL)	Pes (g)	Resultats	
R0	5,84	1.500	0,9	20	0,015	✓	
R0 [baixa]		900	0,9	20	0,015	✗	Problemes analítics, errors a les referències, concentracions massa baixes
		900	0,9	100	0,080	✗	
		800	0,8	20	1	✓	
		800	0,8	100	1	✓	
T8	8,20	1.000	0,9	20	0,015	✓	
R20	0,35	700	0,9	20	0,015	✗	Relació sòlid/líquid massa baixa
		100	0,9	20	0,15	✓	
Torba	47,8	2000	0,9	20	0,010	✓	
Lignit	38,9	20.000	0,9	20	0,0075	✗	Errors als càlculs
		30.000	0,7	20	0,0075	✗	Problemes analítics, estimacions inicials errònies
		300.000	0,9	100	0,003	✗	
		500.000	0,7	20	0,0075	~	Dispersió en els resultats

La representació gràfica de les isoterms per als sediments, la torba i el lignit es mostra a la [Figura 5.4](#). En aquest gràfic s'observa com la isoterma corresponent a la torba va seguir la mateixa tendència que els tres sediments, en els que la sorció que es va observar era més forta

així que augmentava el COT. Tot i que inicialment sembla que l'augment en la sorció no es proporcional a l'augment en el COT, cal tenir en compte que l'escala és logarítmica. Pel que fa al lignit la sorció que va presentar era molt més elevada del que li pertocaria pel seu COT.

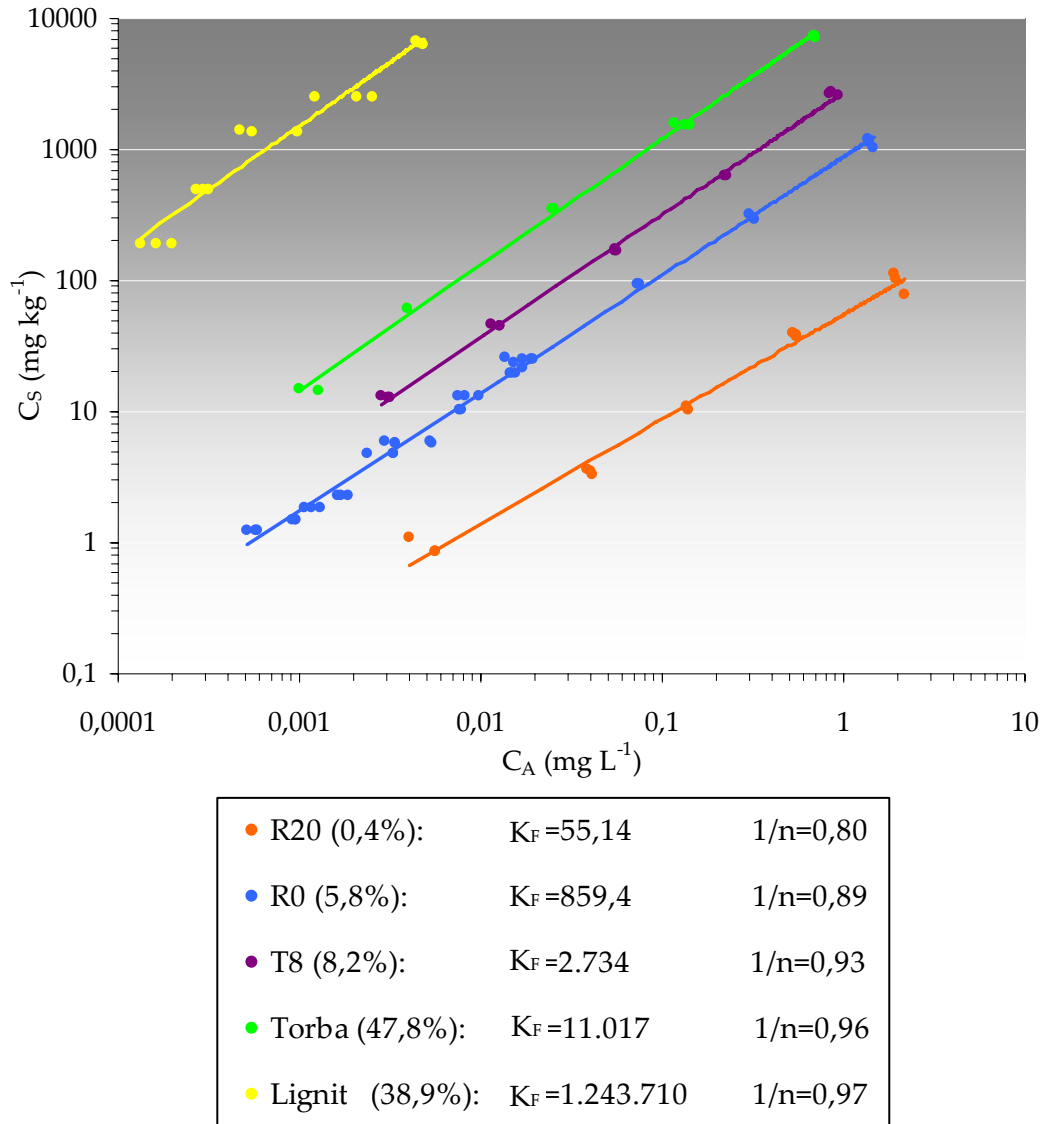


Figura 5.4: Isoterms de sorció de NP per als 5 sorbents estudiats

Per tal de comprovar aquesta relació entre la K_F , com a indicador de la força de la sorció, i el COT, com a mesura de la matèria orgànica del sorbent, es van representar gràficament aquests dos paràmetres i es va ajustar una corba de regressió, tal i com es veu la [Figura 5.5](#). Al fer la representació en forma logarítmica es va obtenir una regressió de tipus potencial amb un coeficient de correlació de 0,979, que en escala logarítmica és una recta. Aquesta correlació es va obtenir però descartant el lignit, ja que, com es pot observar al gràfic, va quedar fora de la regressió, confirmant així el comportament diferenciat d'aquest sorbent respecte als altres.

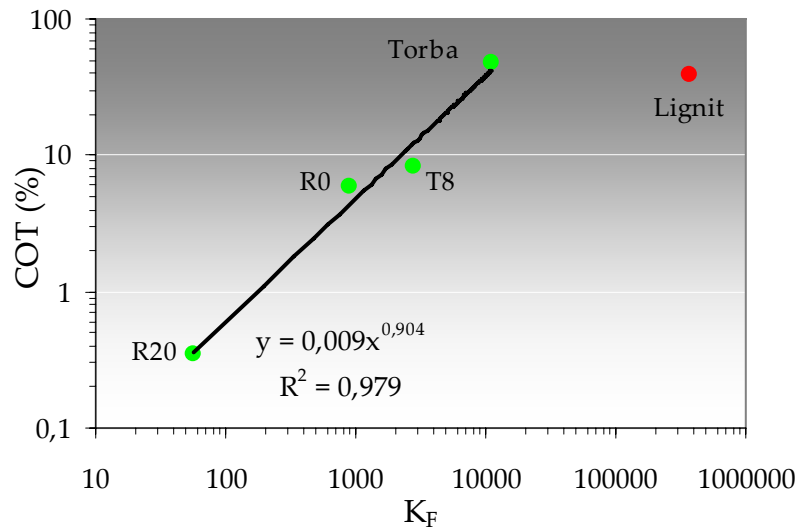


Figura 5.5: Relació del COT i la K_F per al NP dels 5 sorbents utilitzats

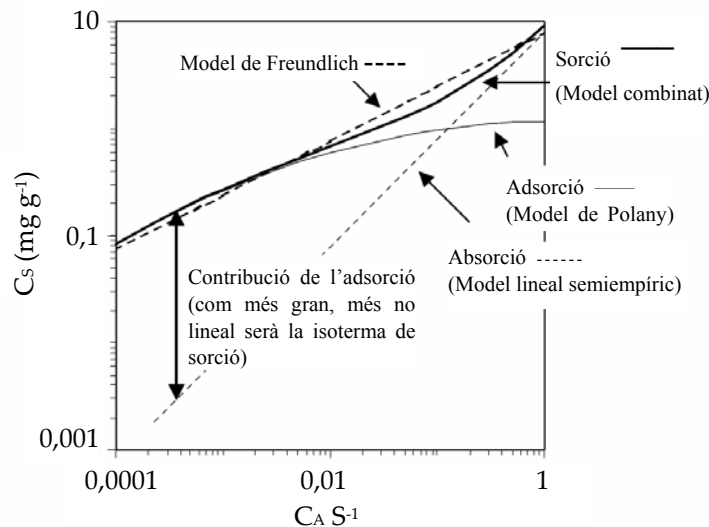
Per a intentar discernir si les dades experimentals obtingudes per al NP durant els assajos de laboratori s'aproximaven més a processos d'adsorció o a processos d'absorció (també anomenada partició) es va aplicar una aproximació semiempírica als resultats obtinguts per a les isoterms de sorció basada en l'estudi d'Allen-King (2002). Aquest model considera la sorció total d'un compost en un sorbent com una superposició de processos d'absorció i adsorció (Xia *et al.*, 1999) en els que, tot i que tenen lloc de forma simultània, normalment s'aprecia que l'adsorció domina a concentracions baixes i l'absorció domina a concentracions més elevades. Aquesta superposició no lineal es pot ajustar en la major part dels casos al model de Freundlich, com s'ha pogut veure anteriorment

El model d'Allen-King es basa en la disgregació dels dos processos de sorció (absorció i adsorció). Per a cadascun d'aquests processos busca la isoterma teòrica que més s'ajusta a les dades experimentals a partir d'altres dades reals d'absorció i adsorció dels compostos d'estudi i diversos paràmetres d'ajust. Per a l'absorció considera que els coeficients de partició de compostos orgànics en materials com els sediments es poden estimar amb relacions semiempíriques basades en la teoria de la solvatació. Existeixen múltiples estudis on s'han determinat aquestes isoterms d'absorció, que normalment s'expressen com una isoterma lineal en escala logarítmica en la que l'absorció és independent de la concentració (Allen-King *et al.*, 2002).

En contrast amb els processos d'absorció, les alteracions tèrmiques de la matèria orgànica creen àrees de gran superfície específica i porositat que promouen l'adsorció no lineal dels compostos. Per a caracteritzar aquesta adsorció s'utilitza el model de Polany-Manes, que deriva

de la teoria de Polany per a l'adsorció d'un sistema en fase gas (Kleineidam *et al.*, 2002) i que es basa en els potencials d'adsorció (Xia *et al.*, 1999).

La Figura 5.6 esquematitza gràficament les aproximacions de l'absorció i l'adsorció del model semiempíric d'Allen-King així com la relació entre el model i la isoterma de Freundlich aplicada a les dades reals. La línia puntejada més gruixuda (----) es correspon amb l'ajust a la isoterma de Freundlich de les dades reals, tal i com s'ha vist a les isoterms presentades fins ara (Figura 5.3). La línia puntejada més prima (.....) és la isoterma d'absorció que més s'aproxima a les dades experimentals, obtinguda de forma teòrica a partir dels coeficients de partició. De la mateixa forma la línia prima (—) és l'aproximació teòrica del model de Polany-Manes per a les dades experimentals. La línia gruixuda (—) és la combinació de l'absorció i d'adsorció teòriques que dona lloc a la isoterma de la sorció total, molt pròxima al model de Freundlich. En el cas presentat en aquesta figura el procés que té més importància és l'adsorció, ja que aquesta isoterma es superposa amb el model de Freundlich mentre que l'absorció incideix mínimament i només a les concentracions més elevades.



Font: Allen-King (2002)

Figura 5.6: Esquema de l'aproximació del model semiempíric combinació d'adsorció i absorció

Per a poder aplicar aquest model de sorció a les dades experimentals obtingudes per al NP en els sediments de l'Ebre i els dos materials orgànics es van seguir els següents passos:

- **1:** El primer pas va ser buscar l'absorció teòrica a partir de les equacions d'absorció per a compostos orgànics existents en la literatura. Amb aquesta finalitat es van

consultar diversos estudis en sediments o sòls (*Karickhoff et al., 1979; Karickhoff, 1981; Sabljic, 1987; Xia, 1998; Seth et al., 1999; Chu et al., 2000*). Atès que no existeix cap coeficient de partició determinat per a APs, es va triar en cadascun dels 5 casos el que donava lloc a una isoterma d'absorció que s'ajustava millor als valors reals.

- **2:** En segon lloc es va calcular l'adsorció teòrica en sediments corresponent a les dades reals en aigua a partir de l'equació de Polany, en la que hi ha diversos paràmetres que cal ajustar, per als que es va fer una estimació inicial.
- **3:** La sorció total teòrica es va calcular com la suma de l'absorció i l'adsorció teòriques obtingudes als punts 1 i 2.
- **4:** Per a determinar el bon ajust del model es va calcular l'error de la manca d'ajust entre el model teòric de sorció total i la sorció real obtinguda dels resultats experimentals.
- **5:** Utilitzant la funció Solver del full de càlcul Excel (Microsoft Corporation, USA) es van ajustar els paràmetres utilitzats com a paràmetres d'ajust del punt 2 per tal que l'error del punt 4 fos el més petit possible. És a dir, es van ajustar els paràmetres de forma que la isoterma de sorció teòrica s'aproximés el màxim possible a les dades reals.
- **6:** A partir de l'equació triada per a l'absorció i els paràmetres determinats per a l'adsorció es va crear un model amb concentracions en aigua i la seva corresponent absorció o adsorció en sediments.
- **7:** Per acabar també es va calcular de forma semiempírica l'adsorció real corresponent als valors de sorció reals menys l'absorció teòrica.

A la [Figura 5.7](#) es mostra la representació gràfica del model d'absorció i adsorció per a cadascun dels casos juntament amb les dades reals i l'adsorció calculada semiempíricament. El bon ajust del model s'aprecia per la superposició de les dades reals amb la línia de la sorció total teòrica. De forma qualitativa es va poder deduir quin procés era el majoritari segons a quina línia s'aproximaven més les dades reals.

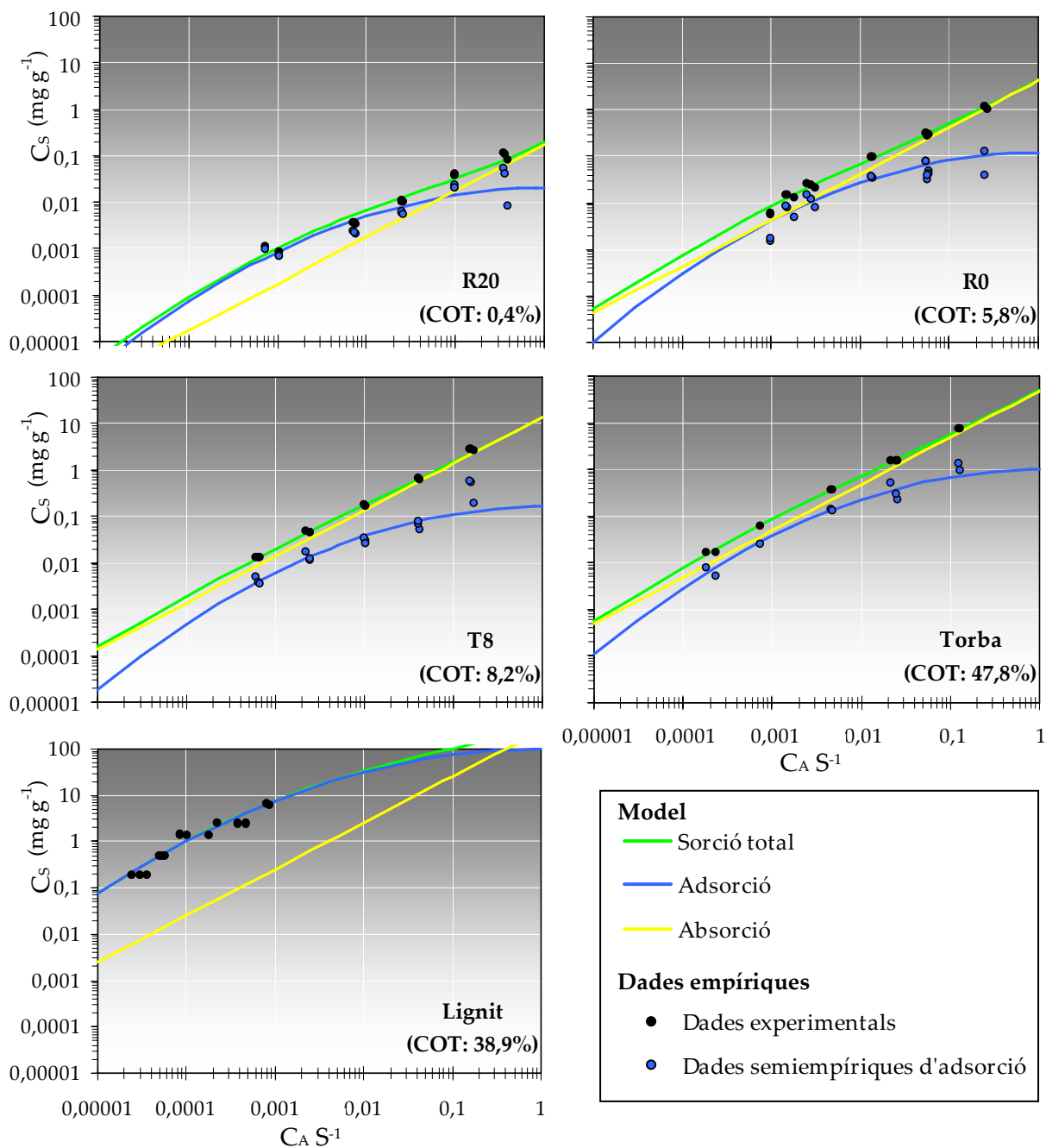


Figura 5.7: Model semiempíric d'adsorció i absorció i dades experimentals per als 5 sorbents utilitzats

En els 4 primers casos, corresponents als 3 sediments i a la torba, el procés predominant era l'absorció i a més, segons augmenta el COT del sorbent la contribució de l'adsorció era cada cop més petita. D'aquesta manera per al sediment R20, amb 0,4% de COT la contribució de l'adsorció va ser significativa però per al T8 o la torba Pahokee, amb 8,2 i 47,8% de COT respectivament, l'adsorció va ser pràcticament nul·la i tota la distribució del contaminant entre la fase aquosa i la sòlida es devia a processos d'absorció. El cas de el lignit és una excepció on

tota la sorció es va deure a processos d'adsorció, a diferència dels altres 4 materials utilitzats. Aquesta diferenciació clara entre els processos que tenen lloc amb el lignit i amb els altres materials pot ser la causa de la falta de correlació entre el COT i la K_F que s'ha vist a la [Figura 5.5](#).

La combinació dels dos processos considerats en aquesta tesi, sorció i degradació, permet estimar el comportament dels contaminants estudiats al medi així com la seva biodisponibilitat, que és la característica que els fa més perjudicials per als organismes vius. A la [Figura 5.8](#) s'esquematitza la influència dels dos processos en la biodisponibilitat d'un compost. Existeixen per tant quatre situacions diferents segons la combinació de la sorció i la degradació que fa que un compost químic sigui més o menys perillós per al medi.

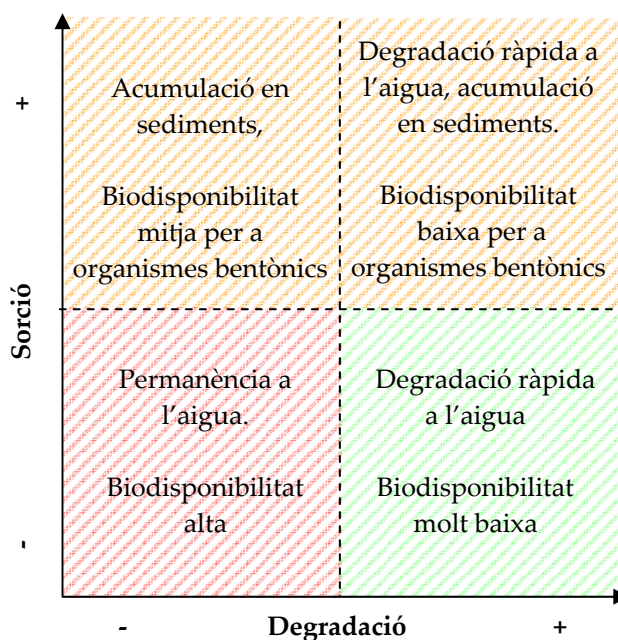


Figura 5.8: Esquema de la influència de la sorció i la degradació en la biodisponibilitat d'un compost

Com hem pogut comprovar, en el cas dels APs es dona una sorció bastant forta però que depèn enormement de les característiques del sorbent, especialment del COT. Per altra banda la fracció que roman a l'aigua pateix una degradació que en redueix la concentració fins a un 64 i 92% respectivament per a NP i OP en 70 dies. Això fa que finalment la fracció biodisponible es vegi reduïda considerablement, però també implica que els sediments acumulin aquests compostos i per tant actuïn com a embornals. Per tant els APs es poden redissoldre en l'aigua si es dona un canvi propici en les condicions per a desencadenar la seva desorció.