CURSO DE POSGRADO · 3ª EDICIÓN

LIMNO.CUENCAS.UY

Eutrofización *y biogeoquímica* ambiental del fósforo.

INICIO

15 de junio
2026

MODALIDAD

Intensivo
Presencial / Distancia

RESPONSABLES

Dr. Guillermo Goyenola
Dra. Mariana Meerhoff
✉ aguadulceuy@gmail.com

PEDECIBA
MEC - UDELAR
BIOLOGÍA
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¿Qué es el fósforo?

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Laboratorio de
Ciencia de Cuencas
y Limnología
del Antropoceno
CATCHMENT SCIENCE · ANTHROPOCENE LIMNOLOGY

DEGA
Departamento de Ecología
y Gestión Ambiental

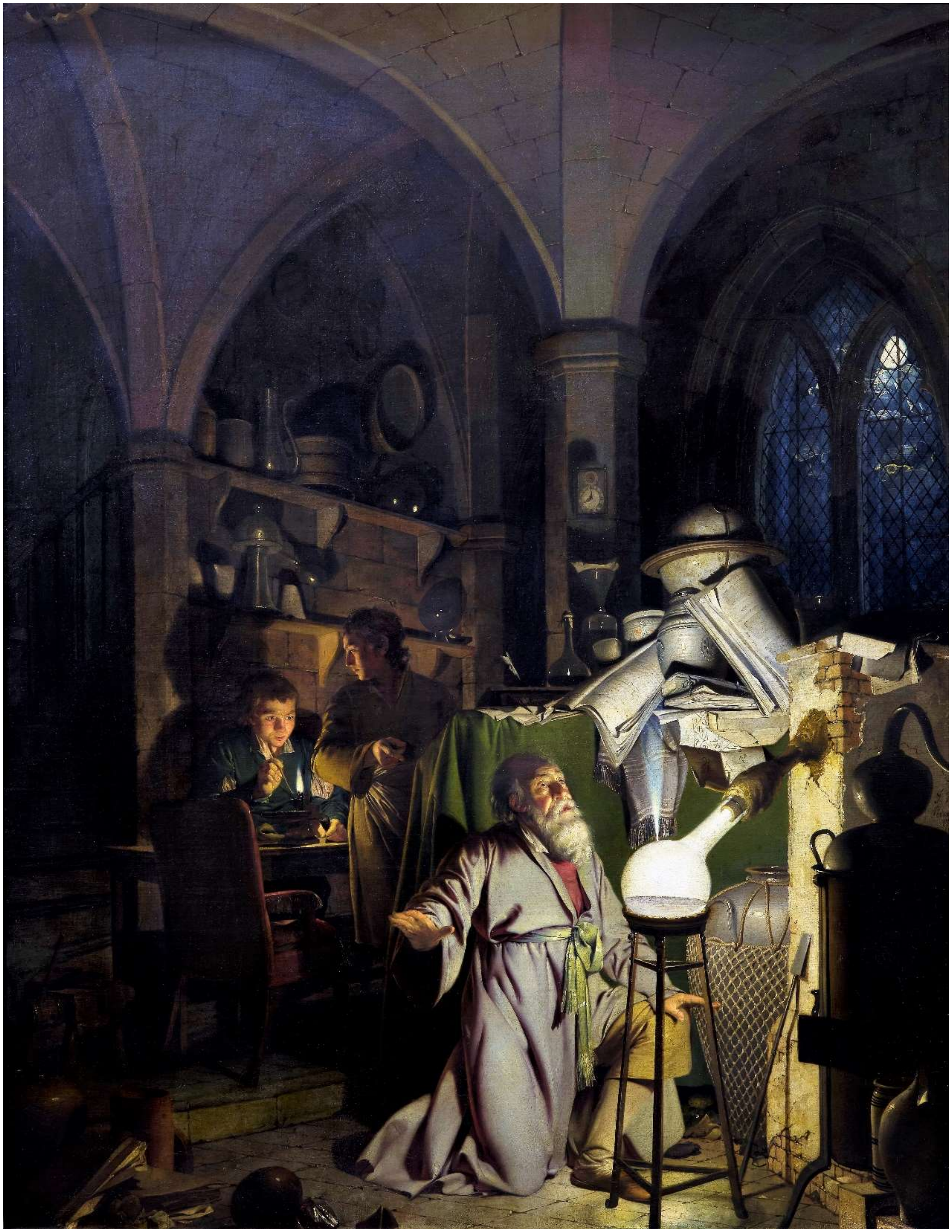
UNIVERSIDAD
DE LA REPÚBLICA
URUGUAY

CURE

Para reproducir los primeros resultados experimentales de este curso, precisaremos acumular unos 5.500 litros de orina humana.

Protocolo práctico

- Deje reposar la orina durante días hasta que desprenda un olor acre.
- Hervir la orina para reducirla a un almíbar espeso.
- Calentar hasta que destile un aceite rojo y extraerlo.
- Dejar enfriar el resto, que está formado por una parte superior esponjosa de color negro y una parte inferior salada.
- Deseche la sal, mezcle el aceite rojo nuevamente con el material negro.
- Calentar fuertemente esa mezcla durante 16 horas.
- Primero se desprenden vapores blancos, luego aceite y finalmente **fósforo**.
- El **fósforo** se puede pasar a agua fría para que se solidifique.



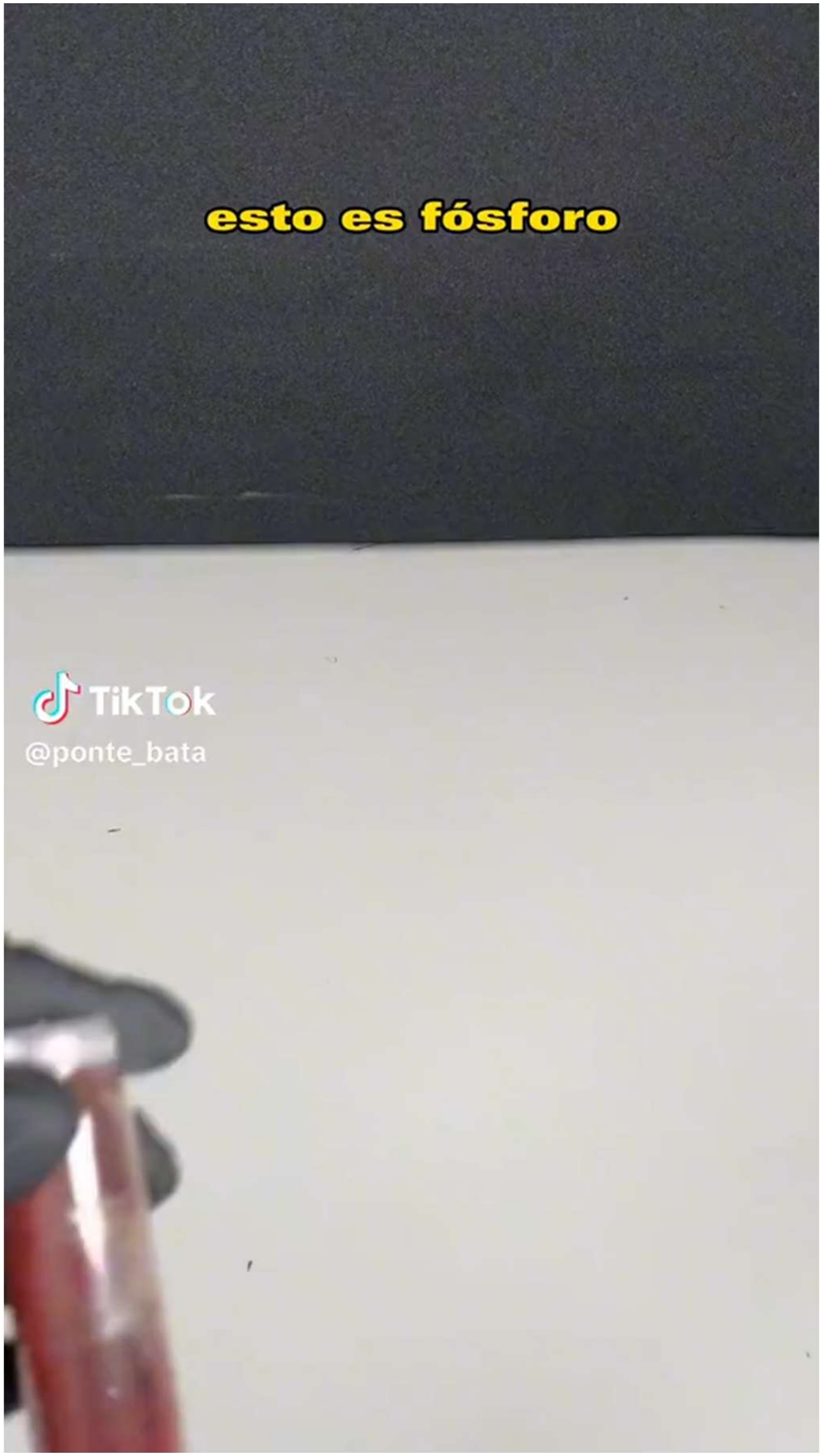
Hennig Brand reza por la exitosa conclusión de su operación luego de descubrir el Fósforo (1669).

El Alquimista, en busca de la Piedra Filosofal (Joseph Wright, 1771)

https://planetario.malargue.gov.ar/2023/09/18/venus-estara-en-su-maximo-brillo-estos-dias/

“Fósforo” en la antigua Grecia era el nombre del planeta Venus.
Sinficaba “luz” (φῶς) + ” portador” (φέρω).

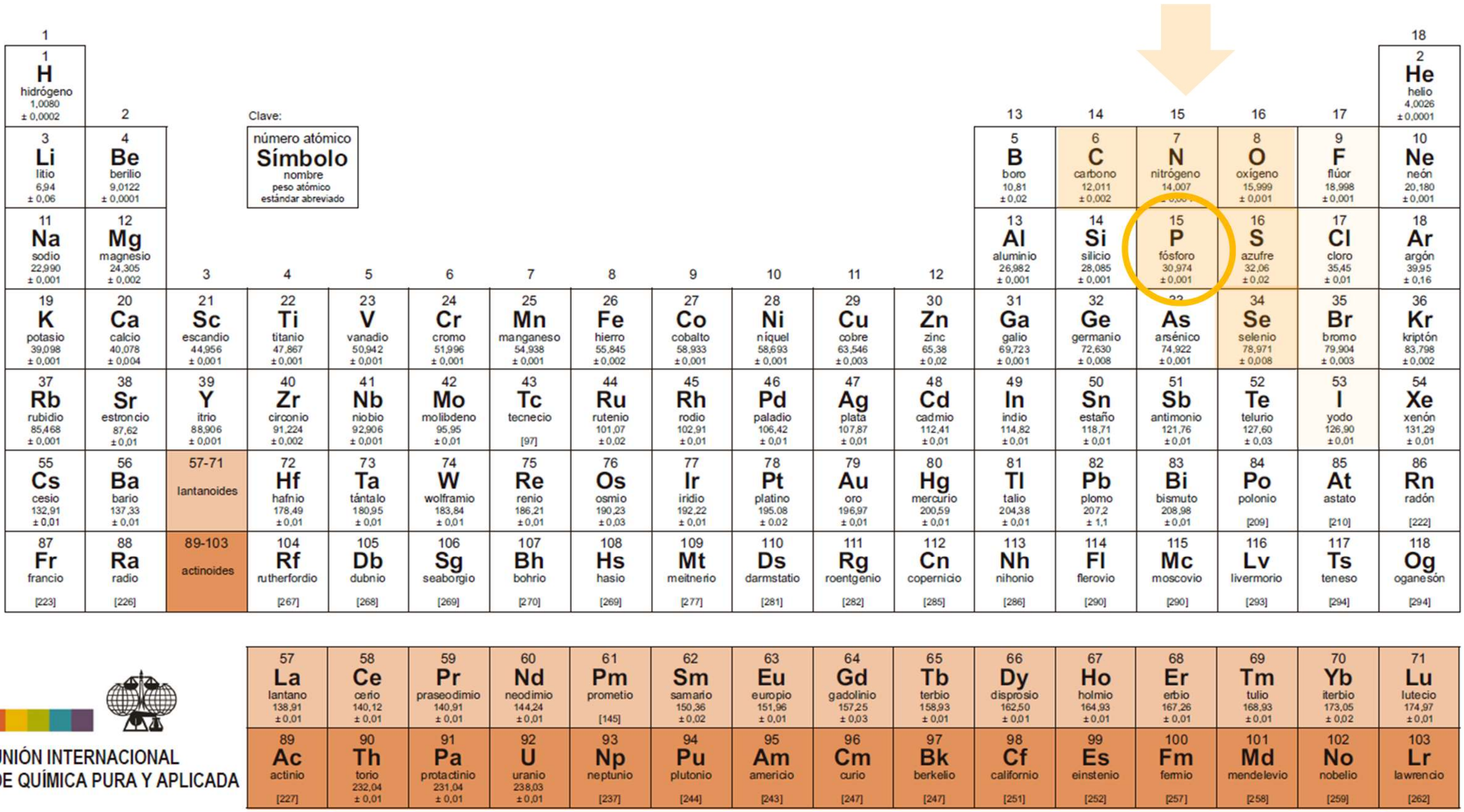
“el milagroso portador de la luz”



https://www.tiktok.com/@ponte_bata/video/7290294387391647009

357 años después del descubrimiento de Hennig Brand...

NO METALES



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** hidrógeno 1,0080 ± 0,0002																	2 **He** helio 4,0026 ± 0,0001
3 **Li** litio 6,94 ± 0,06	4 **Be** berilio 9,0122 ± 0,0001											5 **B** boro 10,81 ± 0,02	6 **C** carbono 12,011 ± 0,002	7 **N** nitrógeno 14,007 [illegible]	8 **O** oxígeno 15,999 ± 0,001	9 **F** flúor 18,998 ± 0,001	10 **Ne** neón 20,180 ± 0,001
11 **Na** sodio 22,990 ± 0,001	12 **Mg** magnesio 24,305 ± 0,002											13 **Al** aluminio 26,982 ± 0,001	14 **Si** silicio 28,085 ± 0,001	15 **P** fósforo 30,974 ± 0,001	16 **S** azufre 32,06 ± 0,02	17 **Cl** cloro 35,45 ± 0,01	18 **Ar** argón 39,95 ± 0,16
19 **K** potasio 39,098 ± 0,001	20 **Ca** calcio 40,078 ± 0,004	21 **Sc** escandio 44,956 ± 0,001	22 **Ti** titanio 47,867 ± 0,001	23 **V** vanadio 50,942 ± 0,001	24 **Cr** cromo 51,996 ± 0,001	25 **Mn** manganeso 54,938 ± 0,001	26 **Fe** hierro 55,845 ± 0,002	27 **Co** cobalto 58,933 ± 0,001	28 **Ni** níquel 58,693 ± 0,001	29 **Cu** cobre 63,546 ± 0,003	30 **Zn** zinc 65,38 ± 0,02	31 **Ga** galio 69,723 ± 0,001	32 **Ge** germanio 72,630 ± 0,008	33 **As** arsénico 74,922 ± 0,001	34 **Se** selenio 78,971 ± 0,008	35 **Br** bromo 79,904 ± 0,003	36 **Kr** kriptón 83,798 ± 0,002
37 **Rb** rubidio 85,468 ± 0,001	38 **Sr** estroncio 87,62 ± 0,01	39 **Y** itrio 88,906 ± 0,001	40 **Zr** circonio 91,224 ± 0,002	41 **Nb** niobio 92,906 ± 0,001	42 **Mo** molibdeno 95,95 ± 0,01	43 **Tc** tecnecio [97]	44 **Ru** rutenio 101,07 ± 0,02	45 **Rh** rodio 102,91 ± 0,01	46 **Pd** paladio 106,42 ± 0,01	47 **Ag** plata 107,87 ± 0,01	48 **Cd** cadmio 112,41 ± 0,01	49 **In** indio 114,82 ± 0,01	50 **Sn** estaño 118,71 ± 0,01	51 **Sb** antimonio 121,76 ± 0,01	52 **Te** telurio 127,60 ± 0,03	53 **I** yodo 126,90 ± 0,01	54 **Xe** xenón 131,29 ± 0,01
55 **Cs** cesio 132,91 ± 0,01	56 **Ba** bario 137,33 ± 0,01	57-71 lantanoides	72 **Hf** hafnio 178,49 ± 0,01	73 **Ta** tántalo 180,95 ± 0,01	74 **W** wolframio 183,84 ± 0,01	75 **Re** renio 186,21 ± 0,01	76 **Os** osmio 190,23 ± 0,03	77 **Ir** iridio 192,22 ± 0,01	78 **Pt** platino 195.08 ± 0,02	79 **Au** oro 196,97 ± 0,01	80 **Hg** mercurio 200,59 ± 0,01	81 **Tl** talio 204,38 ± 0,01	82 **Pb** plomo 207,2 ± 1,1	83 **Bi** bismuto 208,98 ± 0,01	84 **Po** polonio [209]	85 **At** astato [210]	86 **Rn** radón [222]
87 **Fr** francio [223]	88 **Ra** radio [226]	89-103 actinoides	104 **Rf** rutherfordio [267]	105 **Db** dubnio [268]	106 **Sg** seaborgio [269]	107 **Bh** bohrio [270]	108 **Hs** hasio [269]	109 **Mt** meitnerio [277]	110 **Ds** darmstatio [281]	111 **Rg** roentgenio [282]	112 **Cn** copernicio [285]	113 **Nh** nihonio [286]	114 **Fl** flerovio [290]	115 **Mc** moscovio [290]	116 **Lv** livermorio [293]	117 **Ts** teneso [294]	118 **Og** oganesón [294]

Clave:

número atómico
Símbolo
nombre
peso atómico estándar abreviado

57 **La** lantano 138,91 ± 0,01	58 **Ce** cerio 140,12 ± 0,01	59 **Pr** praseodimio 140,91 ± 0,01	60 **Nd** neodimio 144,24 ± 0,01	61 **Pm** prometio [145]	62 **Sm** samario 150,36 ± 0,02	63 **Eu** europio 151,96 ± 0,01	64 **Gd** gadolinio 157,25 ± 0,03	65 **Tb** terbio 158,93 ± 0,01	66 **Dy** disprosio 162,50 ± 0,01	67 **Ho** holmio 164,93 ± 0,01	68 **Er** erbio 167,26 ± 0,01	69 **Tm** tulio 168,93 ± 0,01	70 **Yb** iterbio 173,05 ± 0,02	71 **Lu** lutecio 174,97 ± 0,01
89 **Ac** actinio [227]	90 **Th** torio 232,04 ± 0,01	91 **Pa** protactinio 231,04 ± 0,01	92 **U** uranio 238,03 ± 0,01	93 **Np** neptunio [237]	94 **Pu** plutonio [244]	95 **Am** americio [243]	96 **Cm** curio [247]	97 **Bk** berkelio [247]	98 **Cf** californio [251]	99 **Es** einstenio [252]	100 **Fm** fermio [257]	101 **Md** mendelevio [258]	102 **No** nobelio [259]	103 **Lr** lawrencio [262]

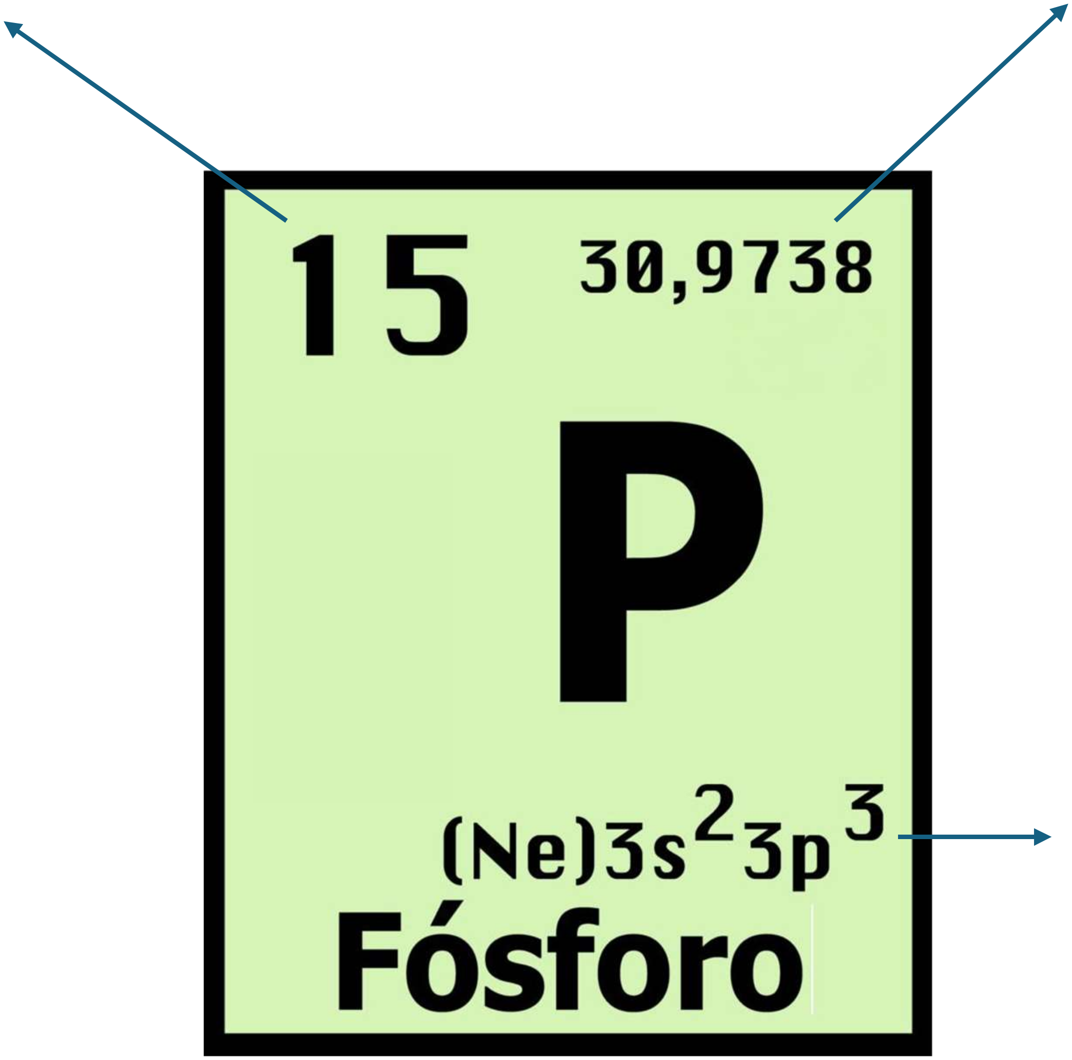
UNIÓN INTERNACIONAL
DE QUÍMICA PURA Y APLICADA

15 protones en su núcleo

masa 31
15 p+ y 16 neutrones

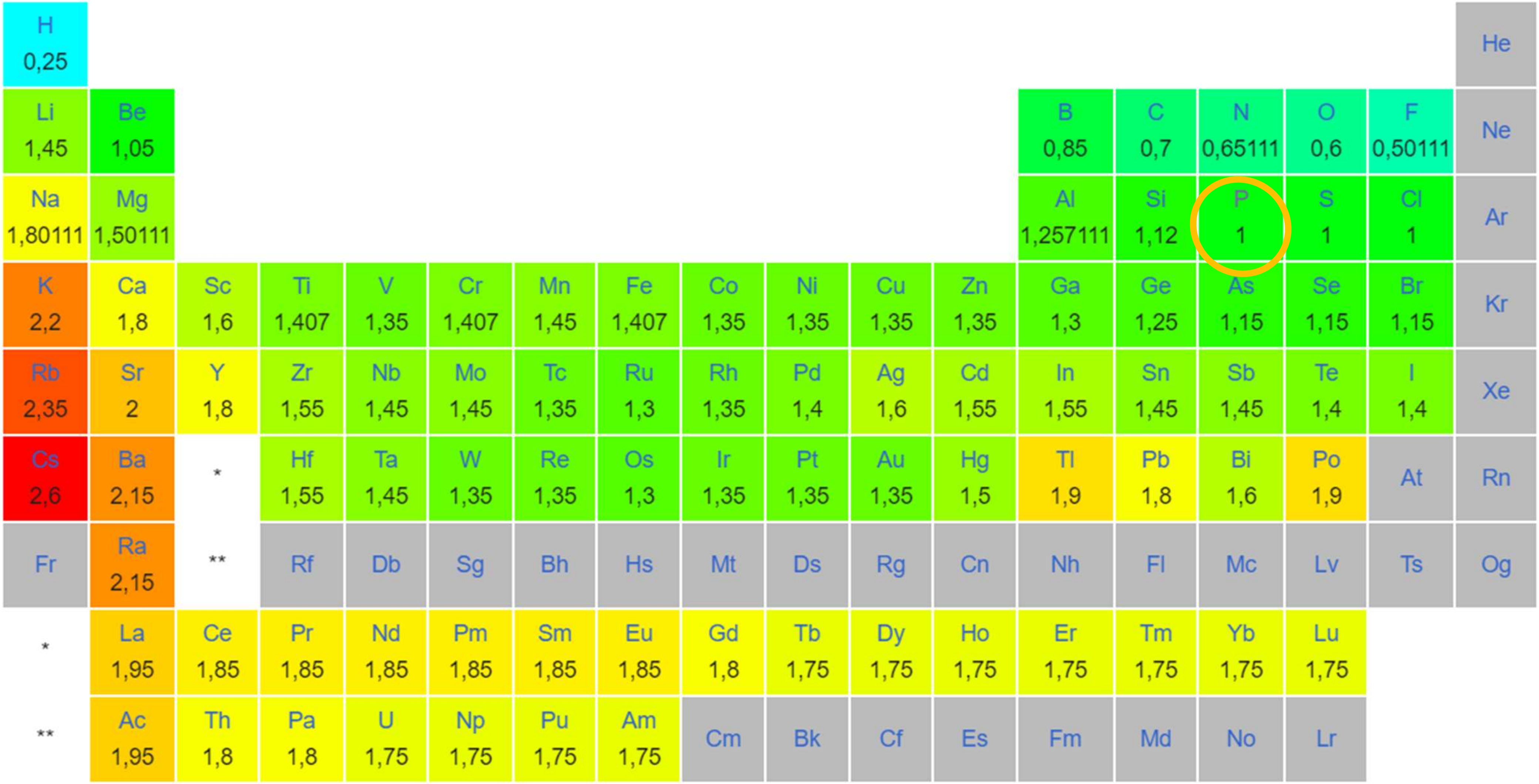
Los 23 isótopos conocidos de P (^{25}P al ^{47}P) tienen períodos de semidesintegración muy breves.

Sólo el ^{31}P es estable y, por lo tanto, está presente en la naturaleza en una abundancia del 100%.



15 e-
5 de valencia

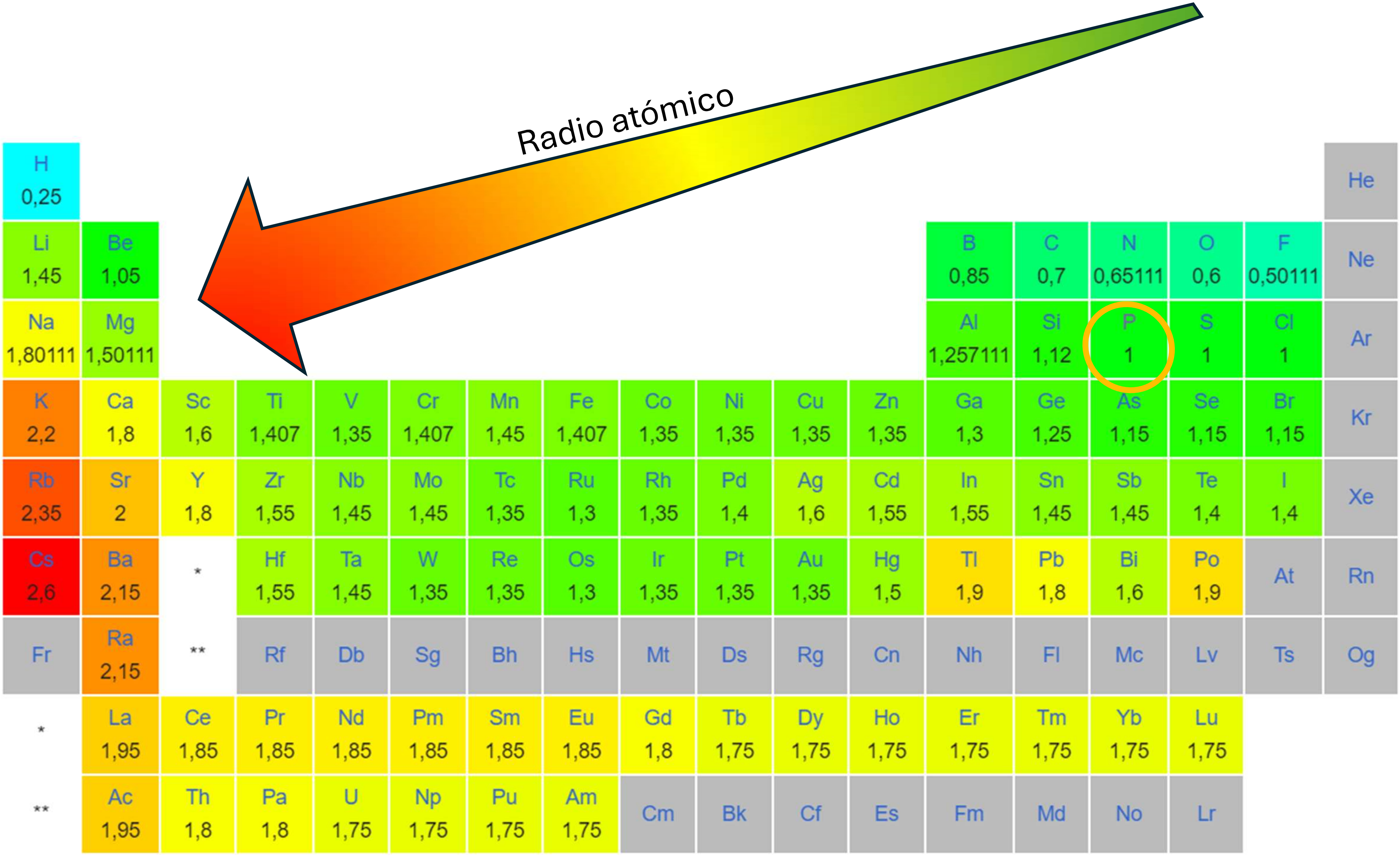
Radio atómico



H 0,25																	He
Li 1,45	Be 1,05											B 0,85	C 0,7	N 0,65111	O 0,6	F 0,50111	Ne
Na 1,80111	Mg 1,50111											Al 1,257111	Si 1,12	P 1	S 1	Cl 1	Ar
K 2,2	Ca 1,8	Sc 1,6	Ti 1,407	V 1,35	Cr 1,407	Mn 1,45	Fe 1,407	Co 1,35	Ni 1,35	Cu 1,35	Zn 1,35	Ga 1,3	Ge 1,25	As 1,15	Se 1,15	Br 1,15	Kr
Rb 2,35	Sr 2	Y 1,8	Zr 1,55	Nb 1,45	Mo 1,45	Tc 1,35	Ru 1,3	Rh 1,35	Pd 1,4	Ag 1,6	Cd 1,55	In 1,55	Sn 1,45	Sb 1,45	Te 1,4	I 1,4	Xe
Cs 2,6	Ba 2,15	*	Hf 1,55	Ta 1,45	W 1,35	Re 1,35	Os 1,3	Ir 1,35	Pt 1,35	Au 1,35	Hg 1,5	Tl 1,9	Pb 1,8	Bi 1,6	Po 1,9	At	Rn
Fr	Ra 2,15	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
*	La 1,95	Ce 1,85	Pr 1,85	Nd 1,85	Pm 1,85	Sm 1,85	Eu 1,85	Gd 1,8	Tb 1,75	Dy 1,75	Ho 1,75	Er 1,75	Tm 1,75	Yb 1,75	Lu 1,75		
**	Ac 1,95	Th 1,8	Pa 1,8	U 1,75	Np 1,75	Pu 1,75	Am 1,75	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

(1 ángstrom = 10^{-10} m = 0,1 nm)

J. C. Slater (1964). «Atomic Radii in Crystals». Journal of Chemical Physics. 41: 3199. doi:10.1063/1.1725697.



H 0,25																	He
Li 1,45	Be 1,05											B 0,85	C 0,7	N 0,65111	O 0,6	F 0,50111	Ne
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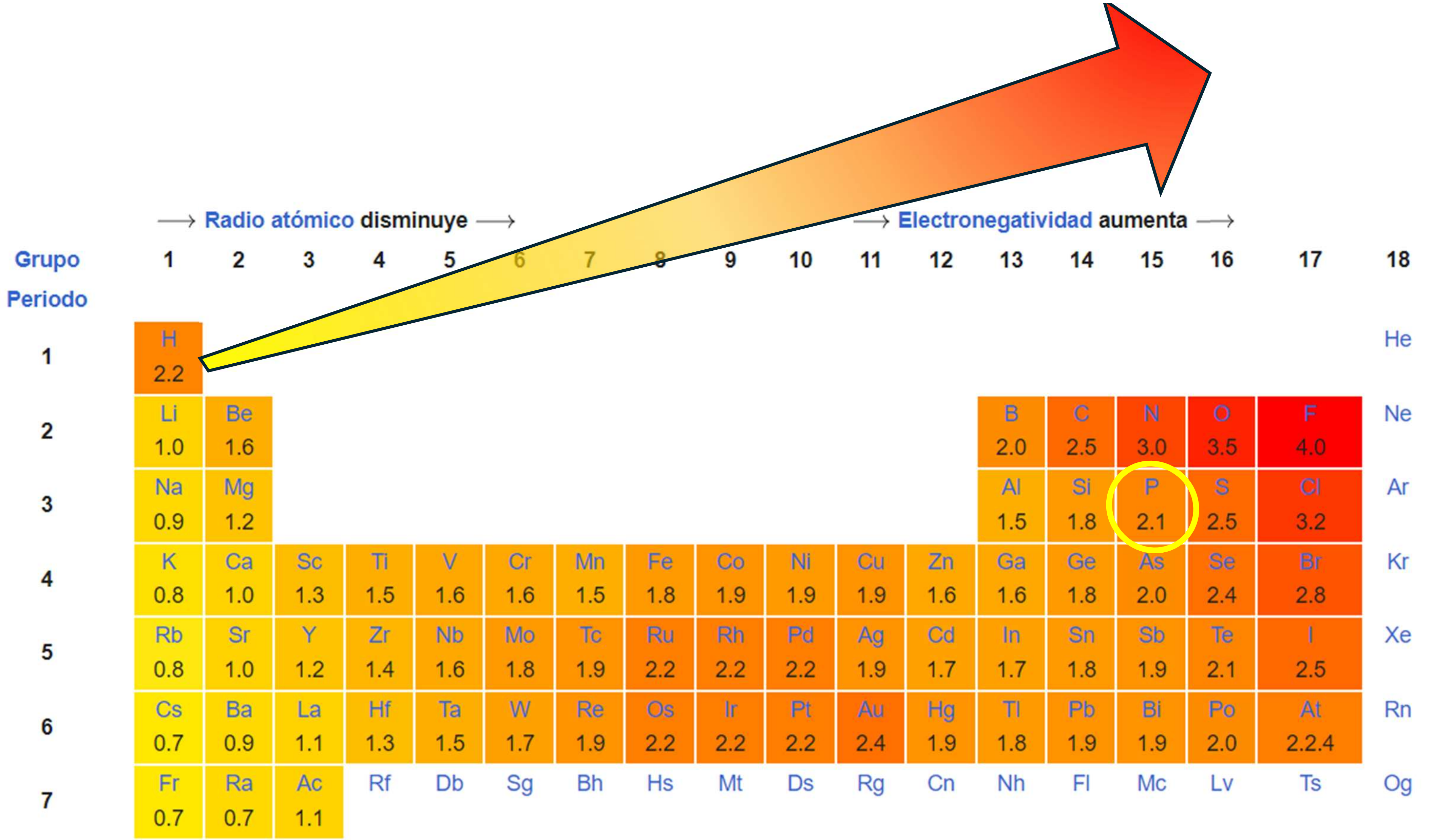
K 2,2	Ca 1,8	Sc 1,6	Ti 1,407	V 1,35	Cr 1,407	Mn 1,45	Fe 1,407	Co 1,35	Ni 1,35	Cu 1,35	Zn 1,35	Ga 1,3	Ge 1,25	As 1,15	Se 1,15	Br 1,15	Kr
Rb 2,35	Sr 2	Y 1,8	Zr 1,55	Nb 1,45	Mo 1,45	Tc 1,35	Ru 1,3	Rh 1,35	Pd 1,4	Ag 1,6	Cd 1,55	In 1,55	Sn 1,45	Sb 1,45	Te 1,4	I 1,4	Xe
Cs 2,6	Ba 2,15	*	Hf 1,55	Ta 1,45	W 1,35	Re 1,35	Os 1,3	Ir 1,35	Pt 1,35	Au 1,35	Hg 1,5	Tl 1,9	Pb 1,8	Bi 1,6	Po 1,9	At	Rn
Fr	Ra 2,15	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
*	La 1,95	Ce 1,85	Pr 1,85	Nd 1,85	Pm 1,85	Sm 1,85	Eu 1,85	Gd 1,8	Tb 1,75	Dy 1,75	Ho 1,75	Er 1,75	Tm 1,75	Yb 1,75	Lu 1,75		
**	Ac 1,95	Th 1,8	Pa 1,8	U 1,75	Np 1,75	Pu 1,75	Am 1,75	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

(1 ángstrom = 10^{-10} m = 0,1 nm)

J. C. Slater (1964). «Atomic Radii in Crystals». Journal of Chemical Physics. 41: 3199. doi:10.1063/1.1725697.



→ Radio atómico disminuye →

→ Electronegatividad aumenta →

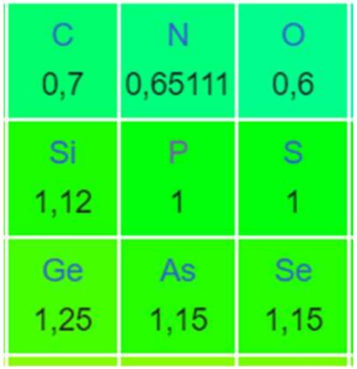
Grupo Periodo	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.2																	He
2	Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
3	Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.2	Ar
4	K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
5	Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
6	Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2.4	Rn
7	Fr 0.7	Ra 0.7	Ac 1.1	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

Tabla Periódica según la electronegatividad usando la escala de Pauling.

N° de electrones de valencia

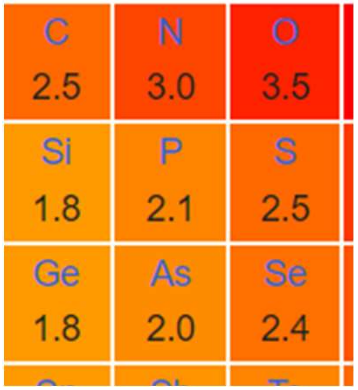
Tipo y cantidad de enlaces

3 para completar el "octete"



C 0,7	N 0,65111	O 0,6
Si 1,12	P 1	S 1
Ge 1,25	As 1,15	Se 1,15

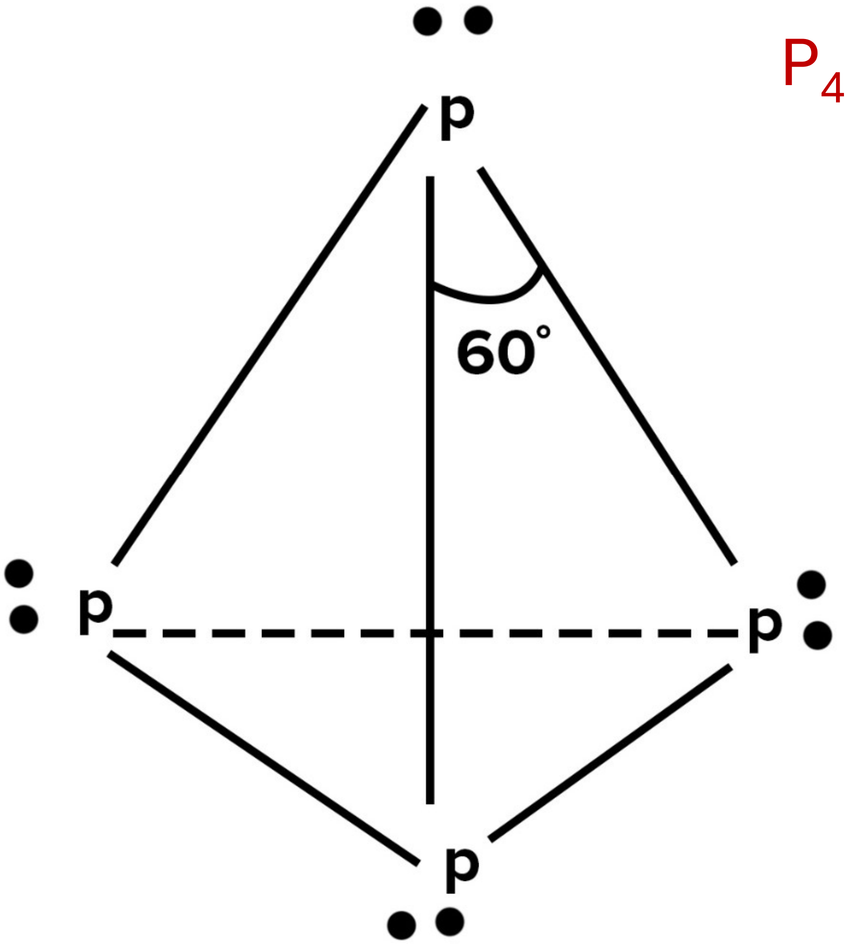
Radio atómico



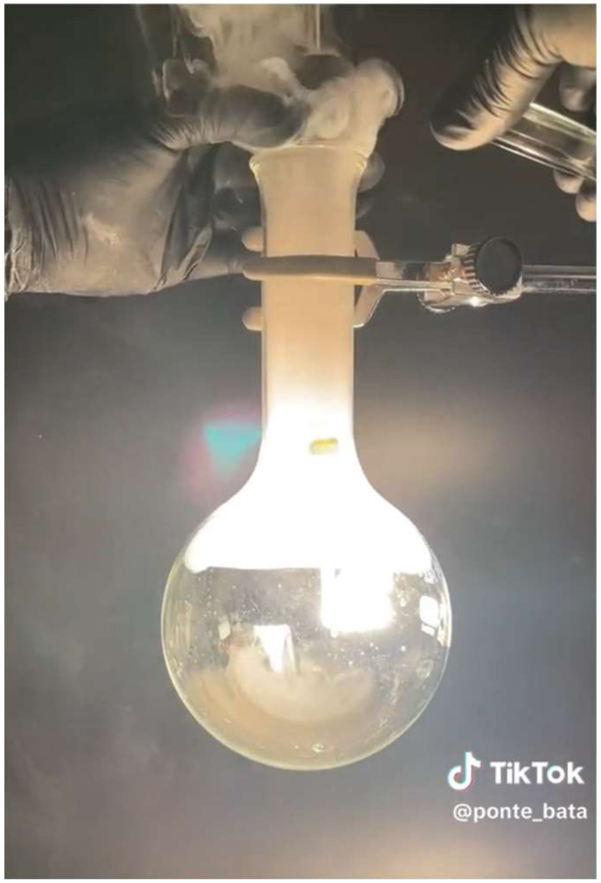
C 2.5	N 3.0	O 3.5
Si 1.8	P 2.1	S 2.5
Ge 1.8	As 2.0	Se 2.4

Electronegatividad

Fósforo blanco



P_4



A pesar de su origen etimológico,

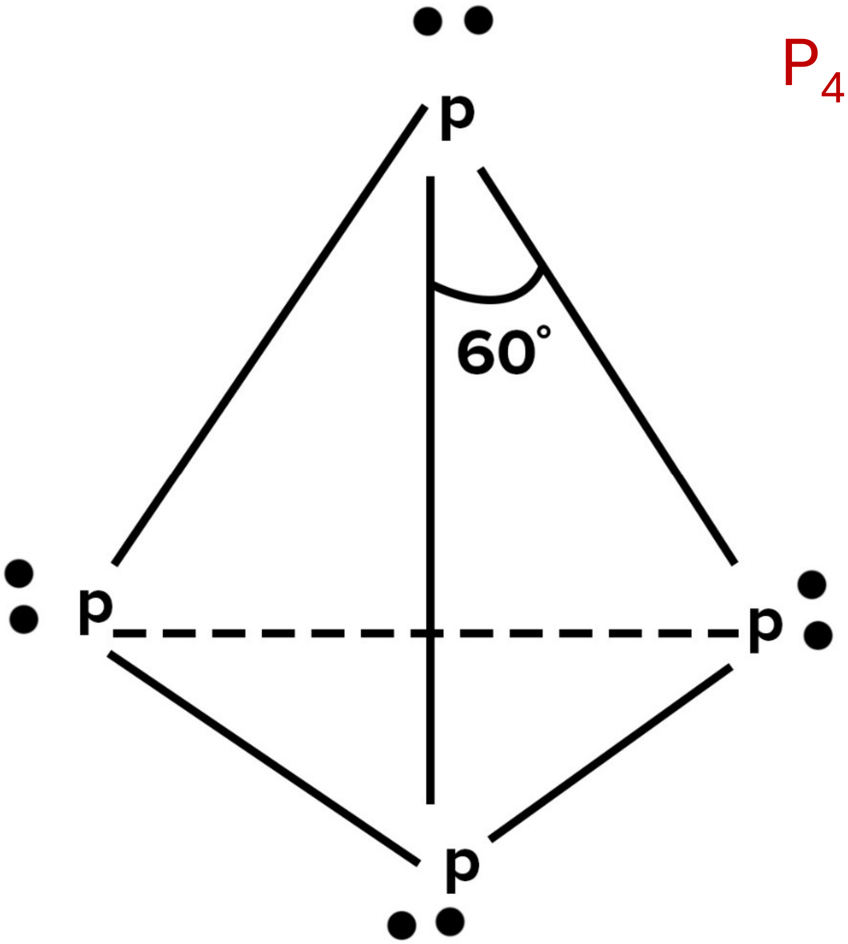
la emisión de luz por el fósforo no ocurre por **fosforescencia**

(RAE: luminiscencia que permanece algún tiempo al cesar la causa que la produce)

sino **quimioluminiscencia**

(resplandor debido a una reacción química en frío - oxidación)

Fósforo blanco

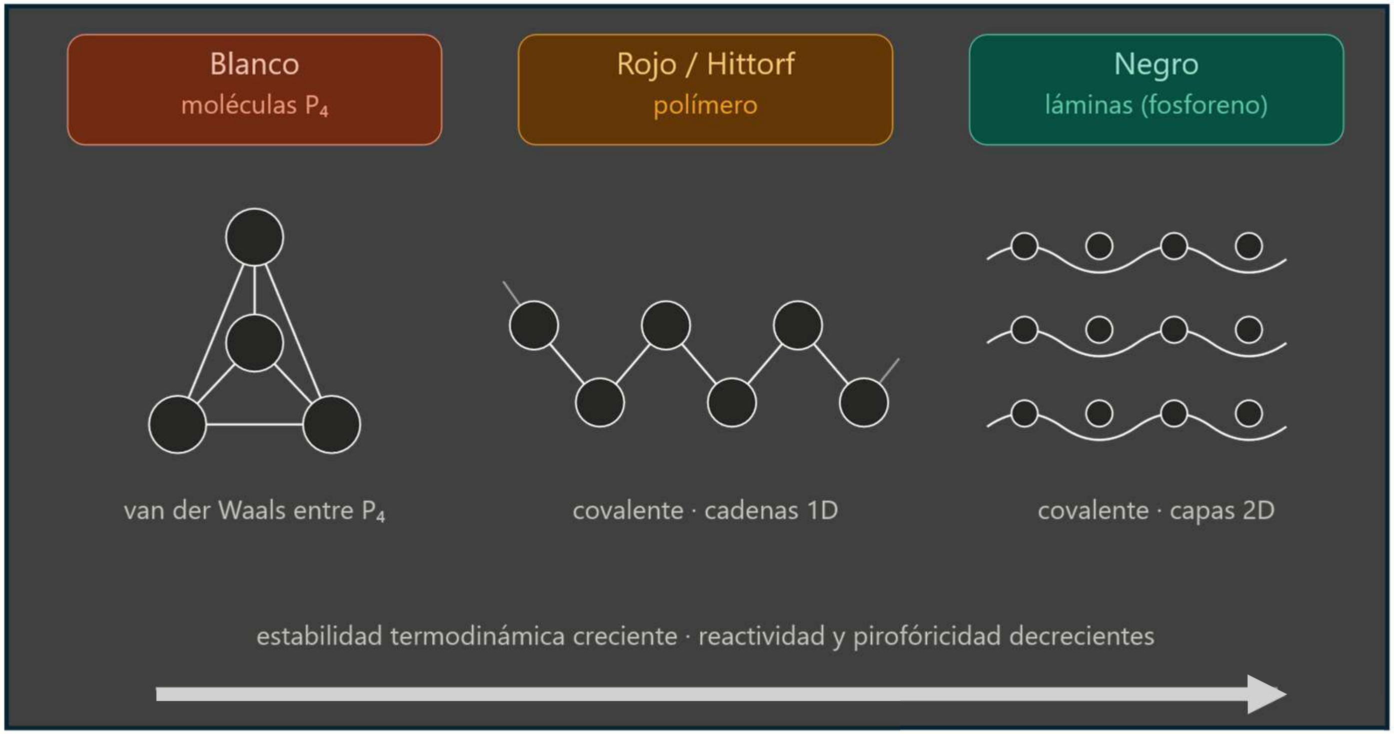


P_4

¡Muy reactivo!
(oxidable)

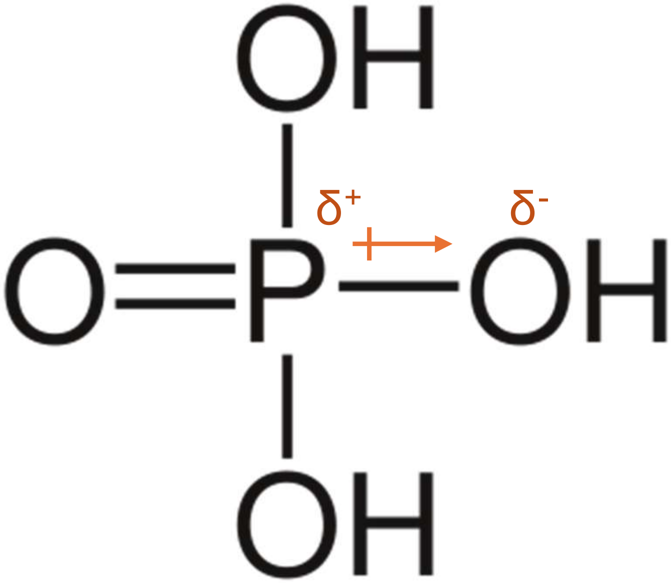
Alótropos

Distintas formas estructurales en que puede existir un **mismo elemento químico**, diferenciándose en cómo se enlazan o se ordenan sus átomos.

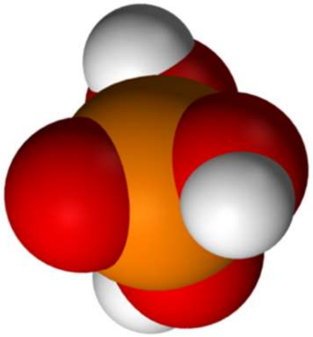


Formas químicas presentes en la biósfera

FORMAS OXIDADAS


$$\mathrm{O{=}P(OH)_3}$$

Ácido fosfórico



C	N	O
2.5	3.0	3.5
Si	P	S
1.8	2.1	2.5

Ácido fosfórico

Fosfato de dihidrógeno

$$H_3PO_{4\,(s)} + H_2O_{(l)} \rightleftharpoons H_3O^{+}{}_{(aq)} + H_2PO_4^{-}{}_{(aq)}$$

Fosfato de
dihidrógeno

Ácido fosfórico

$$H_3PO_{4(s)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + H_2PO_4^-{}_{(aq)}$$

$$H_2PO_4^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + HPO_4^{-2}{}_{(aq)}$$

Fosfato de dihidrógeno

Ácido fosfórico

$$H_3PO_{4\,(s)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + H_2PO_4^-{}_{(aq)}$$

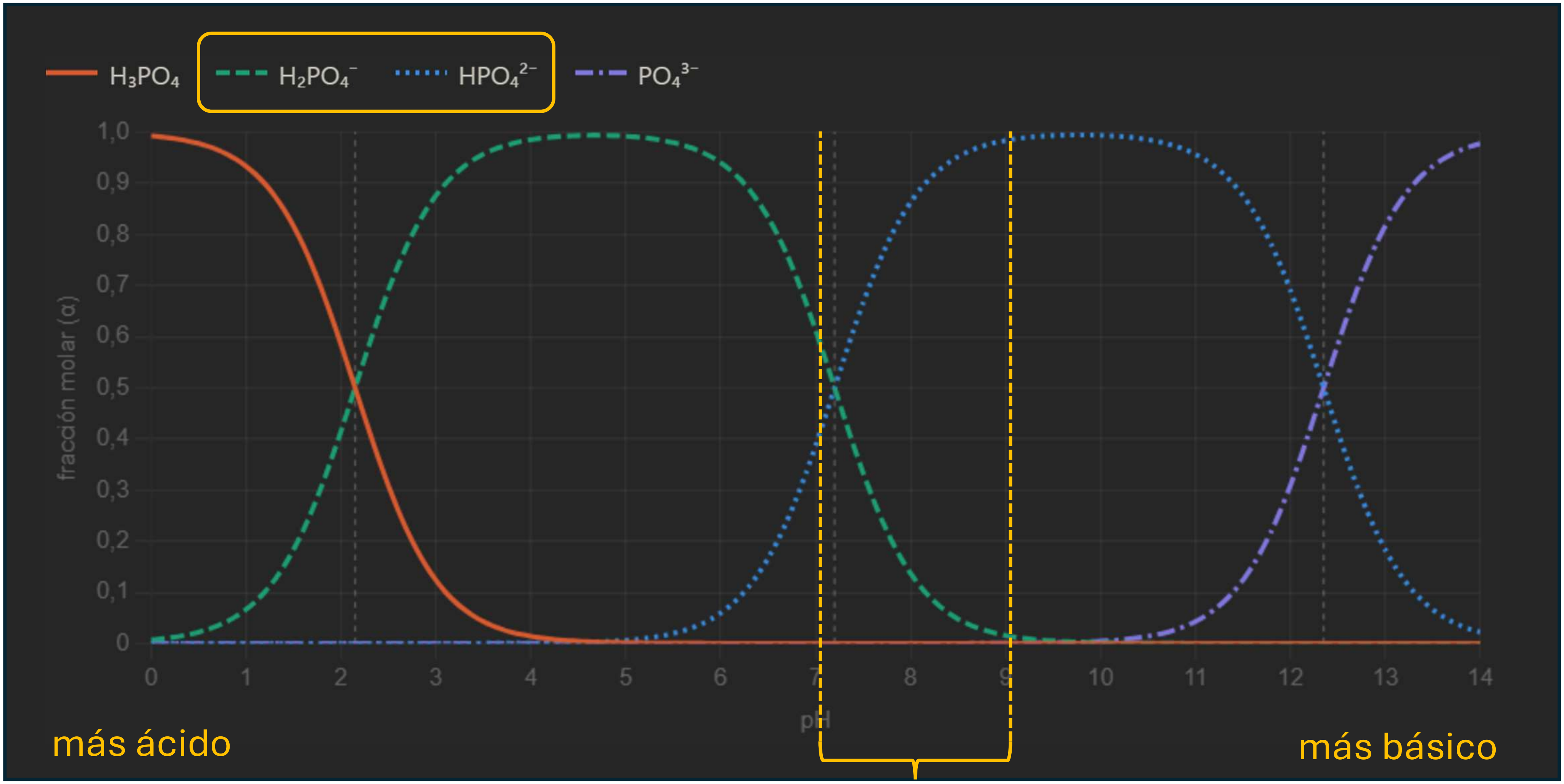
$$H_2PO_4^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + HPO_4^{-2}{}_{(aq)}$$

$$HPO_4^{-2}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + PO_4^{-3}{}_{(aq)}$$

Fosfato

De todas estas, ¿en qué forma es más probable encontrarlo en solución acuosa?

Formas químicas presentes en la biósfera



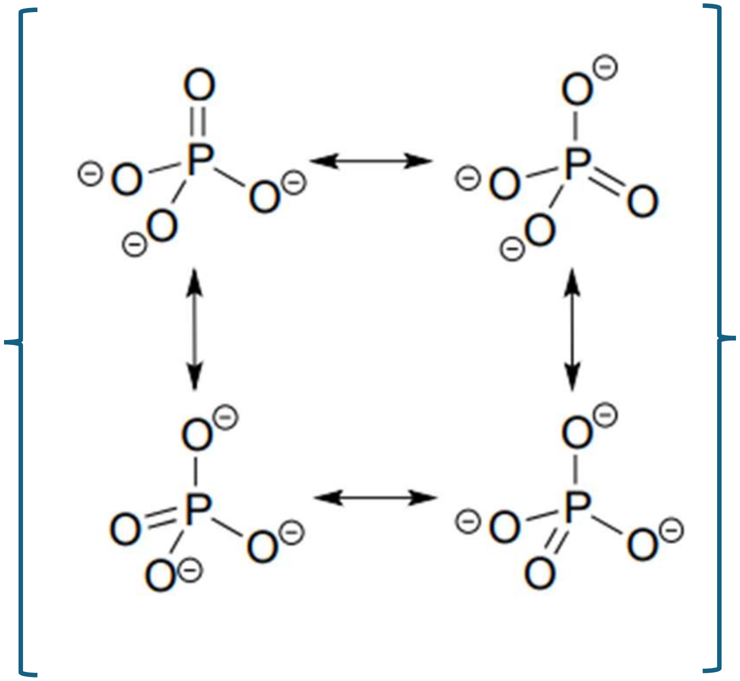
Rango típico de pH en ecosistemas acuáticos

Cuando se hace referencia al **fosfato inorgánico libre en disolución**, no se especifica el estado de protonación.

Es decir, es la suma de las especies $H_2PO_4^-$ + HPO_4^{2-} y trazas de H_3PO_4 y PO_4^{3-}.

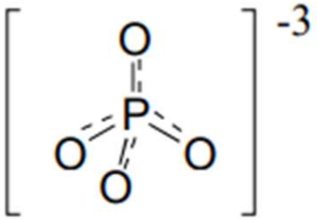
Fosfato (inorgánico) (P_i)

El fosfato es una estructura estable en solución acuosa.
¿Cómo logra estabilidad con tal concentración de carga negativa?



Mesomería

(resonancia)



- Electrones π deslocalizados.
Los 4 enlaces P-O son idénticos de orden > 1.

- Las 3 cargas están distribuidas entre los 4 átomos de oxígeno.

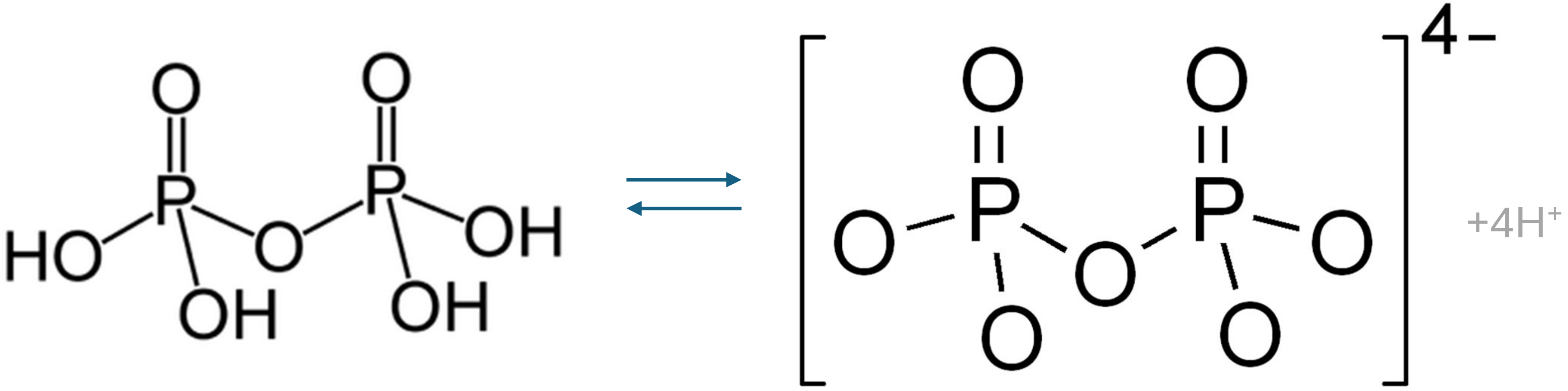
- Soluble en agua: solvente polar + formación de enlaces de hidrógeno.

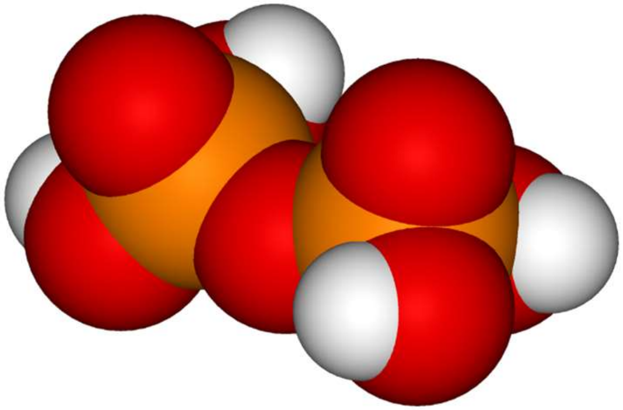
Formas químicas presentes en la biósfera

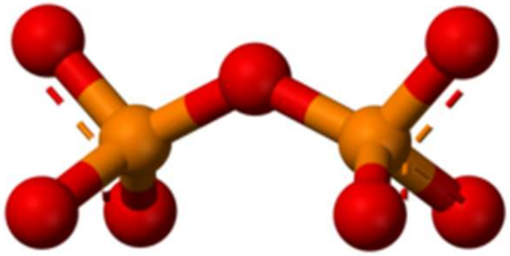
POLÍMEROS

ácido difosfórico
o
pirofosfórico

Pirofosfato
(PPi)





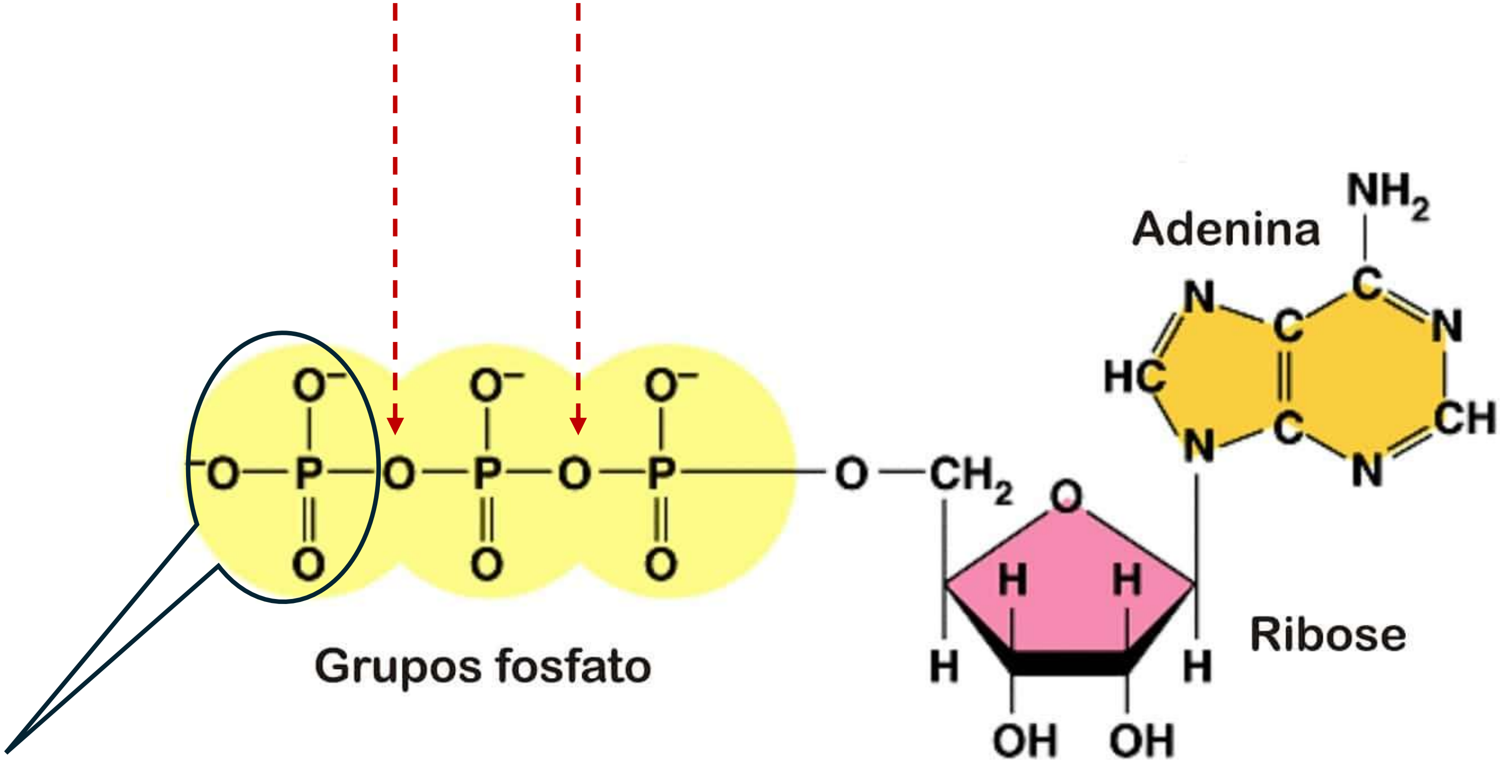


Formas químicas presentes en la biósfera

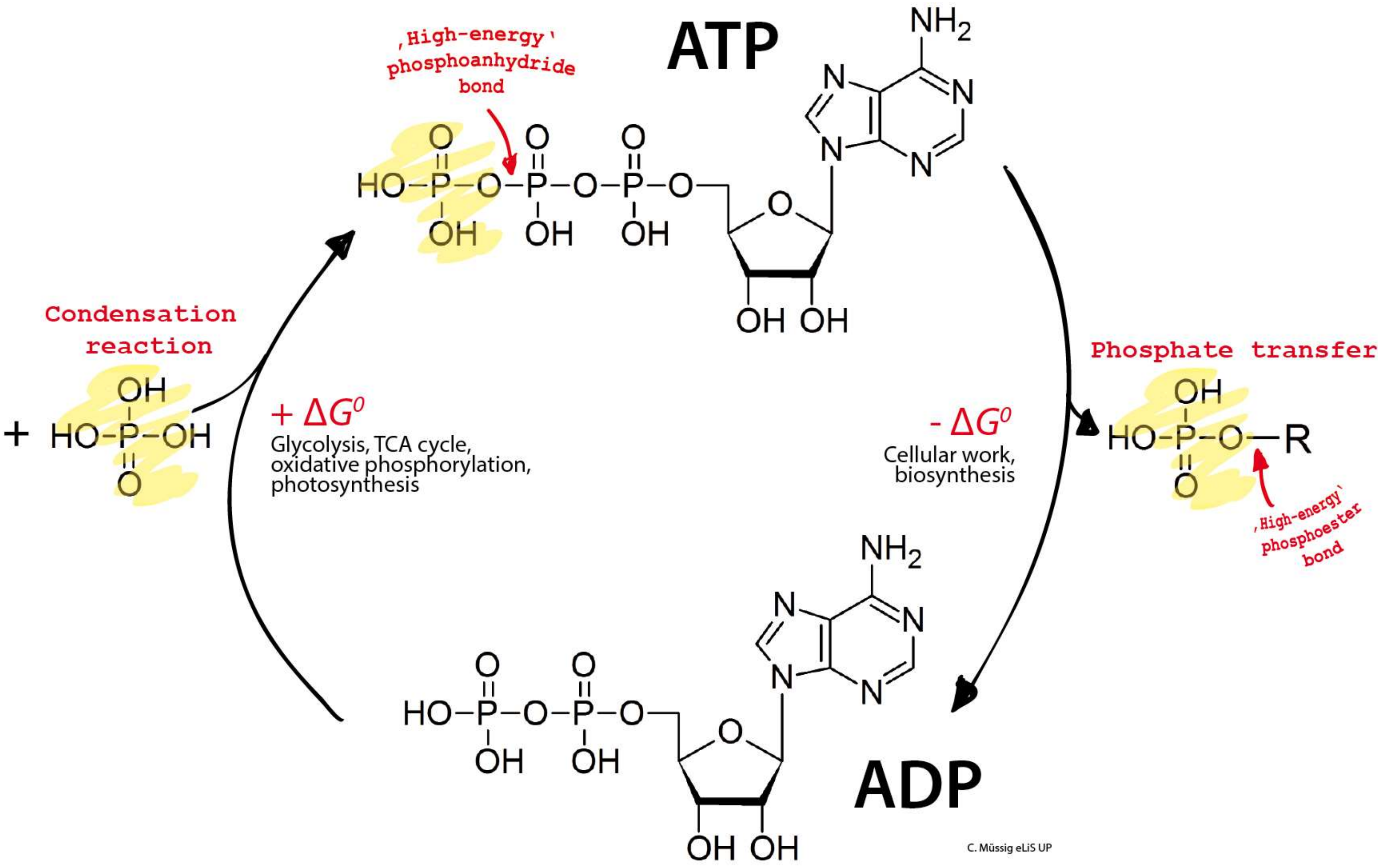
POLÍMEROS

ATP: Adenosina trifosfato

Intermediario metabólico universal de transferencia de energía libre.



fosforilo



‚High-energy' phosphoanhydride bond

Condensation reaction

+ ΔG^0

Glycolysis, TCA cycle, oxidative phosphorylation, photosynthesis

Phosphate transfer

- ΔG^0

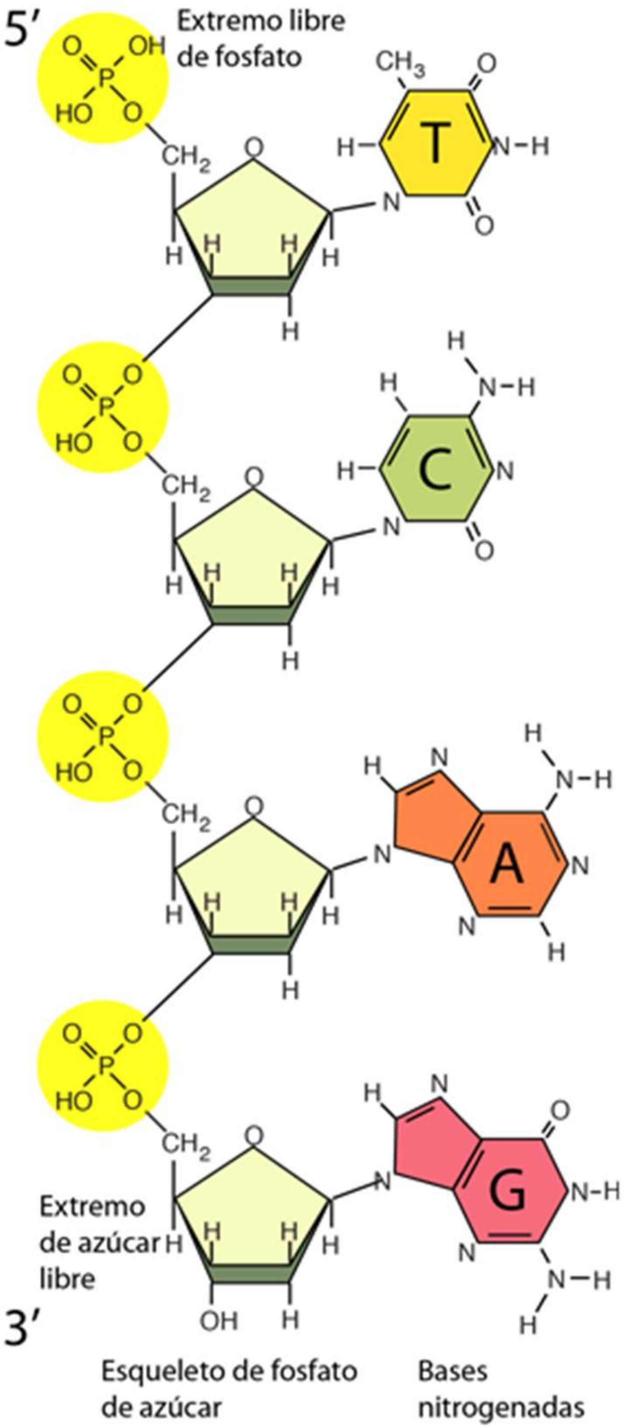
Cellular work, biosynthesis

‚High-energy' phosphoester bond

C. Müssig eLiS UP

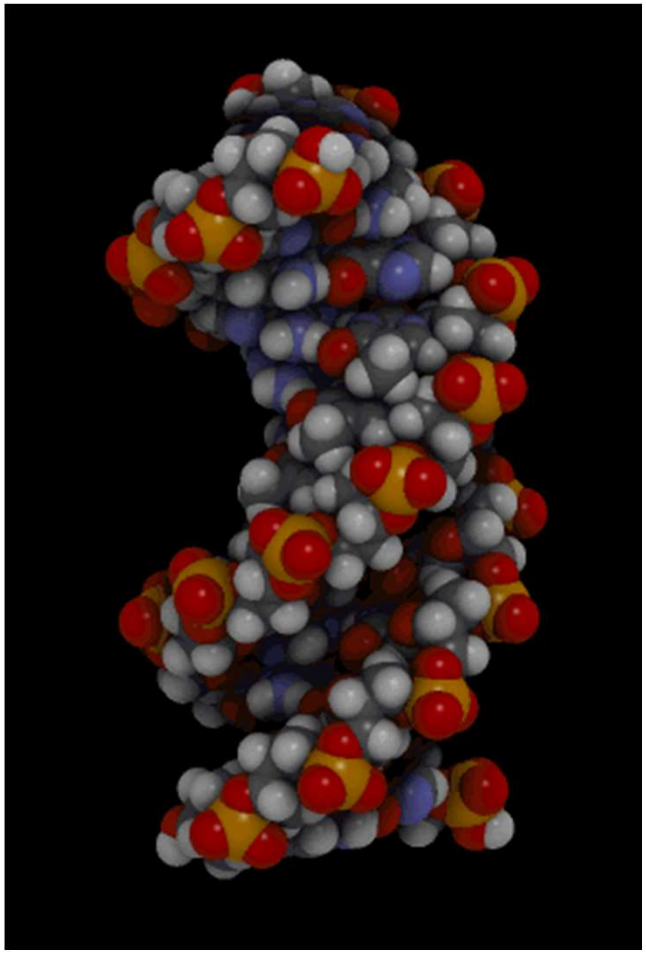
ADN

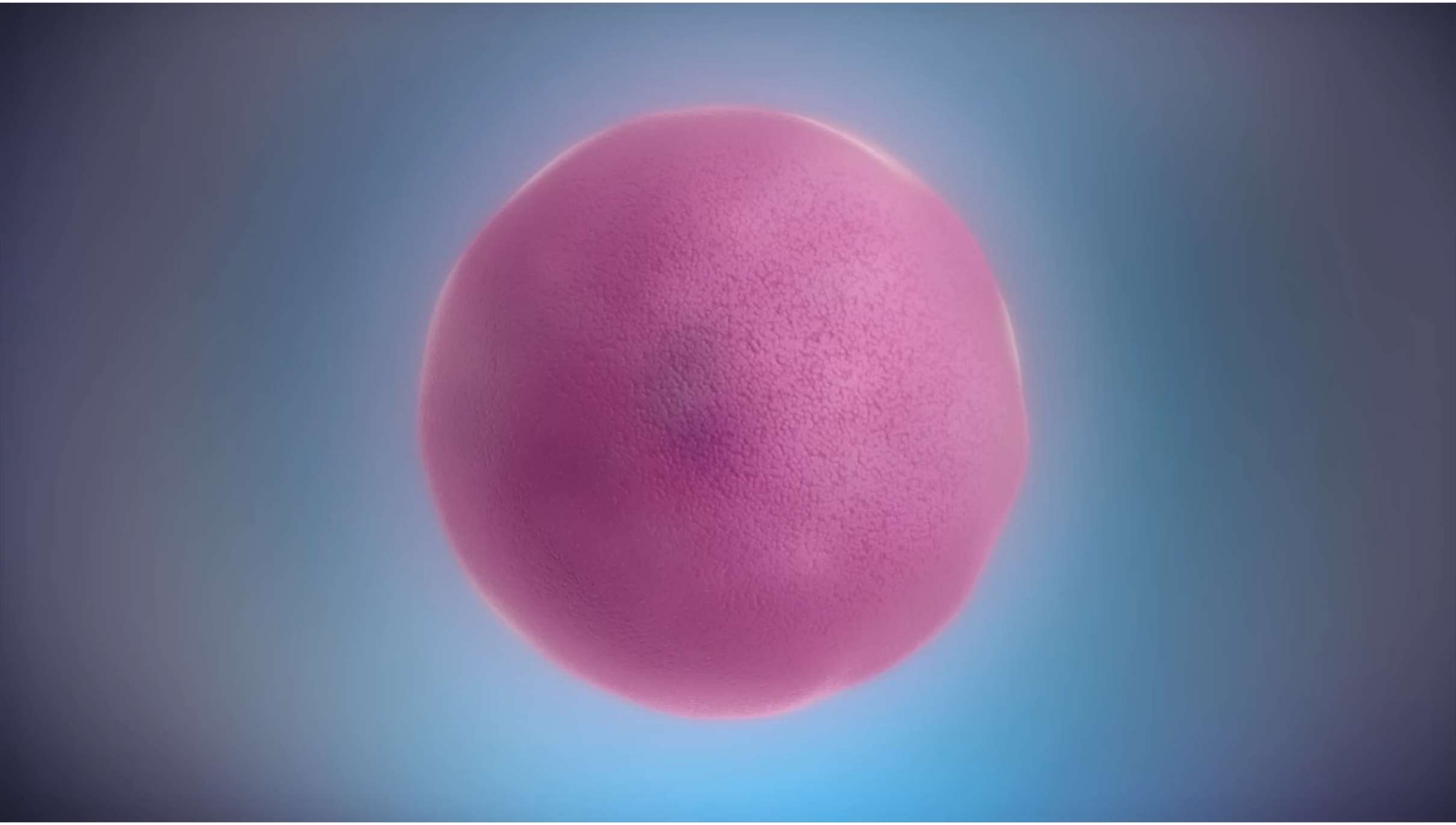
El P es fundamental para la arquitectura biológica.



base de la memoria

ADN

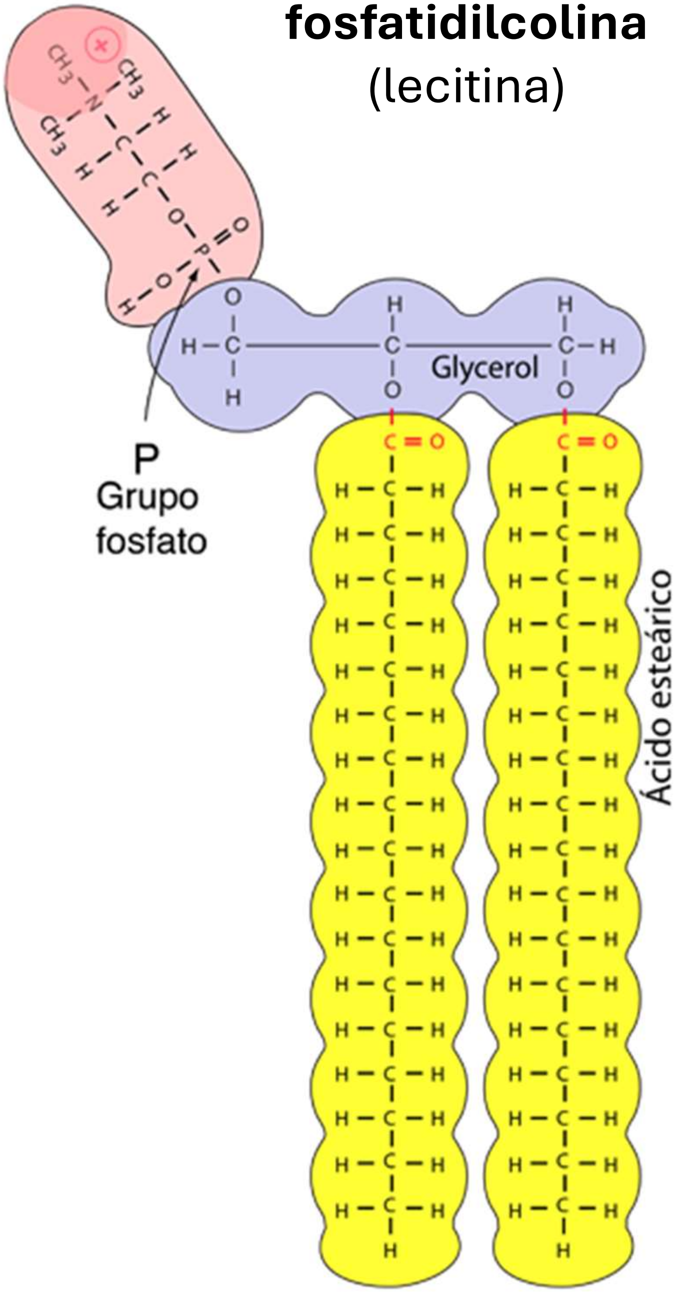




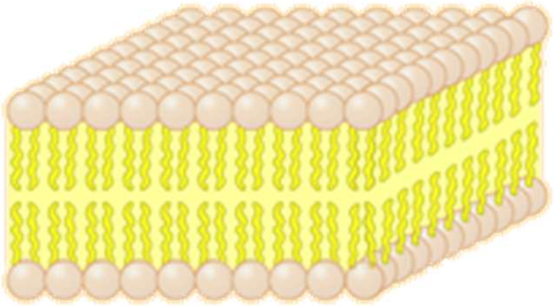
Replicación del ADN - 3D

https://www.youtube.com/watch?v=TNKWgcFPHqw&ab_channel=yourgenome

Fosfolípidos



fosfatidilcolina
(lecitina)

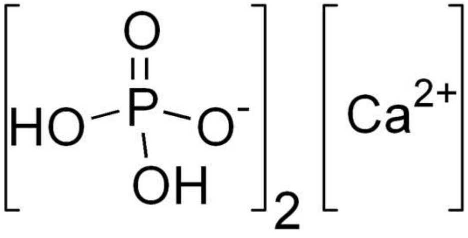


Bicapas lipídicas
Membranas

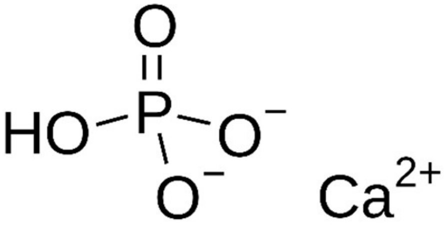
Creador de compartimentos.

ESTRUCTURAS CRISTALINAS

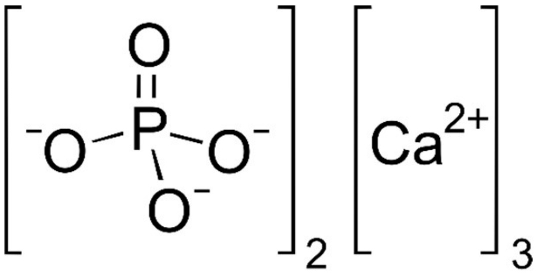
Fosfato de calcio



Fosfato diácido de calcio.



Fosfato ácido de calcio



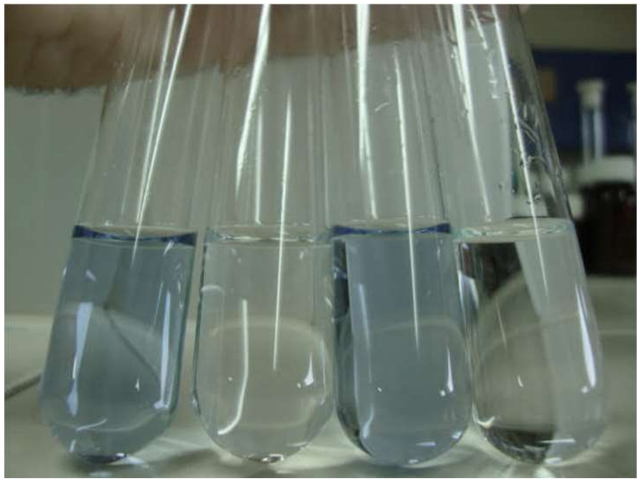
Fosfato de tricalcio
$Ca_3(PO_4)_2$

hidroxiapatita

$Ca_5(PO_4)_3(OH)$

Estructuras de soporte.

Fosfato por doquier



Desde el punto de vista ambiental,
lo relevante es la cantidad de P

El método mide la cantidad de fosfato, pero el
resultado se expresa en función de la cantidad de P

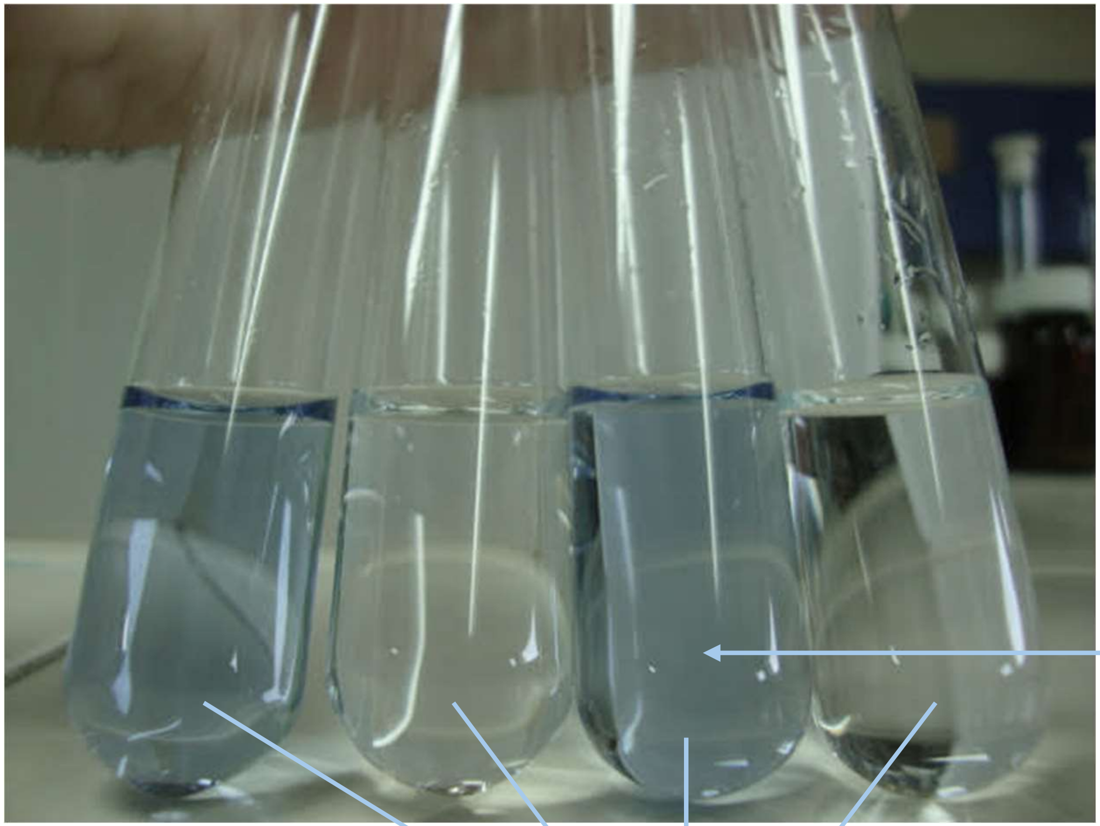
P / PO_4 = 30,97 / 94,97 ≈ 0,326 — el P es el 32,6 % de la masa del fosfato.

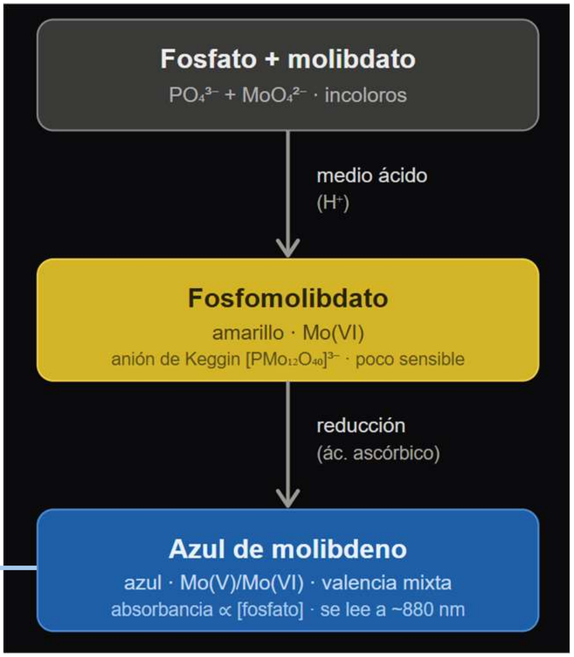
Fósforo inorgánico disuelto
(DIP)
Conceptualmente lo más cercano a P_i en el léxico acuático.
NO ES MEDIBLE.

Fósforo Reactivo Soluble/Disuelto
(PRS o PRD/ SRP o DRP)
Es una aproximación operativa al fosfato disuelto (expresado como P).
El P_i puede sobreestimarse porque el ataque ácido del método hidroliza parte del P orgánico lábil y libera P adsorbido.

Fósforo Total
(PT o TP)

Estrategia analítica





Fosfato + molibdato

PO_4^{3-} + MoO_4^{2-} · incoloros

medio ácido
(H^+)

Fosfomolibdato

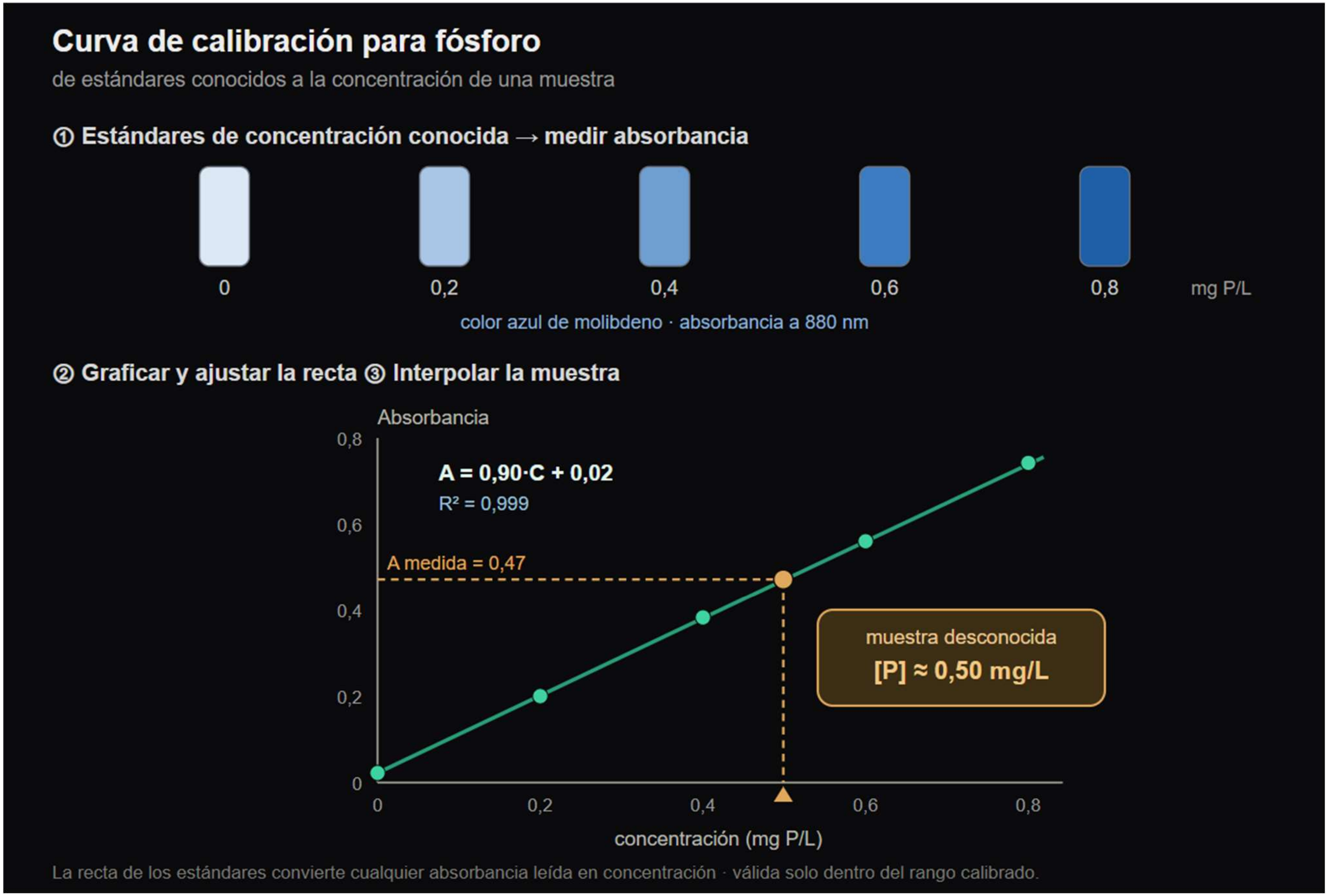
amarillo · Mo(VI)
anión de Keggin $[PMo_{12}O_{40}]^{3-}$ · poco sensible

reducción
(ác. ascórbico)

Azul de molibdeno

azul · Mo(V)/Mo(VI) · valencia mixta
absorbancia ∝ [fosfato] · se lee a ~880 nm

Absorbancia a 880 nm (NIR)



Curva de calibración para fósforo

de estándares conocidos a la concentración de una muestra

① Estándares de concentración conocida → medir absorbancia

color azul de molibdeno · absorbancia a 880 nm

② Graficar y ajustar la recta ③ Interpolar la muestra

$A = 0{,}90 \cdot C + 0{,}02$

$R^2 = 0{,}999$

muestra desconocida

[P] ≈ 0,50 mg/L

La recta de los estándares convierte cualquier absorbancia leída en concentración · válida solo dentro del rango calibrado.

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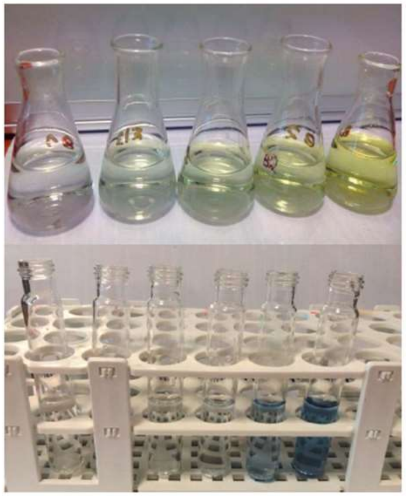
Procedimientos para la determinación de Nutrientes en en muestras de agua y sedimentos



Ecología y Rehabilitación de Sistemas Acuáticos - CURE / UDELAR

Compilado, revisado y complementado por Claudia Fosalba, Franco Teixeira de Mello, Guillermo Goyenola, Virginia Fleitas. Versión 29/08/2022

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Claudia Fosalba

Laboratory of Excellence

CURE Maldonado

This laboratory has been recognized by ERA as a Laboratory of Excellence for achieving 100% acceptable data in the

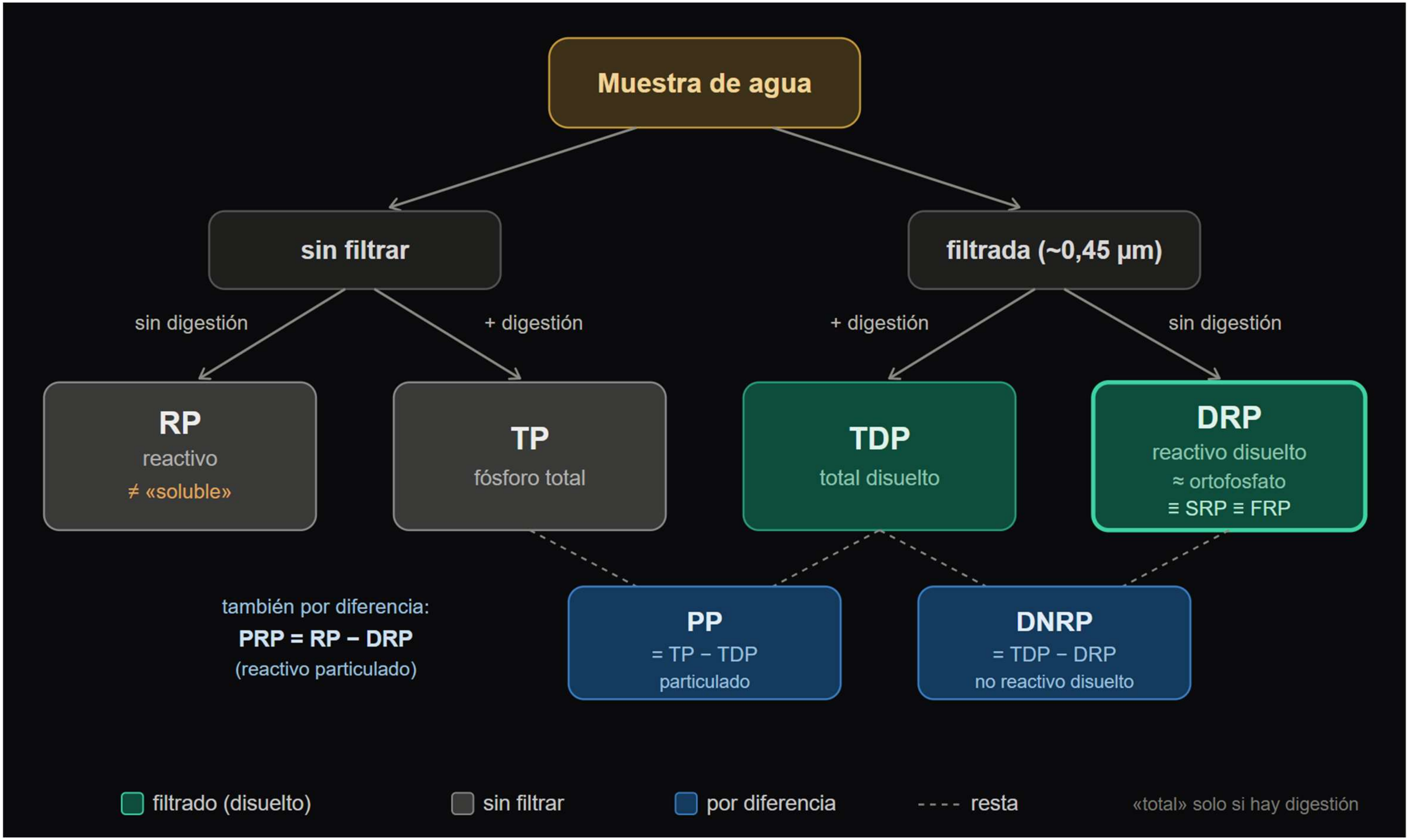
July 2018 WP ERA Proficiency Testing Round 282

which included 918 participating laboratories. This achievement is a demonstration of the superior quality of this laboratory in evaluation of the analyte(s) listed below.

Total phosphorus as P
ortho-Phosphate as P

ERA
A Waters Company

Matthew Seebeck, *Quality Officer*



Muestra de agua

sin filtrar

filtrada (~0,45 µm)

sin digestión

+ digestión

+ digestión

sin digestión

RP
reactivo
≠ «soluble»

TP
fósforo total

TDP
total disuelto

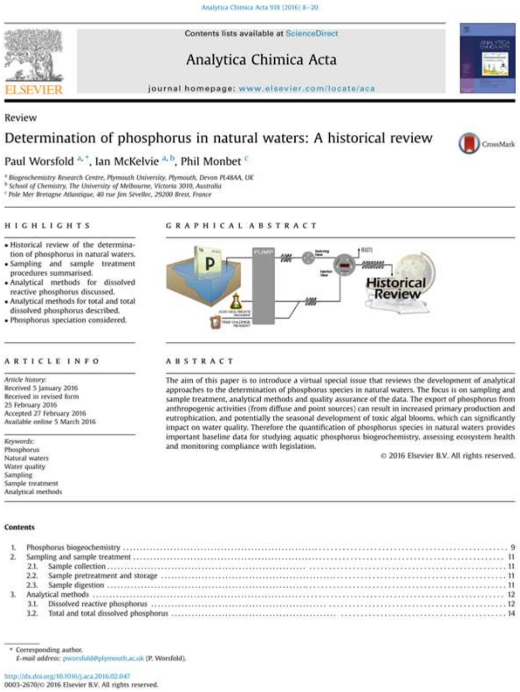
DRP
reactivo disuelto
≈ ortofosfato
≡ SRP ≡ FRP

también por diferencia:
PRP = RP − DRP
(reactivo particulado)

PP
= TP − TDP
particulado

DNRP
= TDP − DRP
no reactivo disuelto

🟩 filtrado (disuelto)
⬛ sin filtrar
🟦 por diferencia
- - - - resta
«total» solo si hay digestión



Analytica Chimica Acta 918 (2016) 8–20

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Review

Determination of phosphorus in natural waters: A historical review

Paul Worsfold [a,*], Ian McKelvie [a,b], Phil Monbet [c]

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HIGHLIGHTS

- Historical review of the determination of phosphorus in natural waters.
- Sampling and sample treatment procedures summarised.
- Analytical methods for dissolved reactive phosphorus discussed.
- Analytical methods for total and total dissolved phosphorus described.
- Phosphorus speciation considered.

GRAPHICAL ABSTRACT

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ABSTRACT

The aim of this paper is to introduce a virtual special issue that reviews the development of analytical approaches to the determination of phosphorus species in natural waters. The focus is on sampling and sample treatment, analytical methods and quality assurance of the data. The export of phosphorus from anthropogenic activities (from diffuse and point sources) can result in increased primary production and eutrophication, and potentially the seasonal development of toxic algal blooms, which can significantly impact on water quality. Therefore the quantification of phosphorus species in natural waters provides important baseline data for studying aquatic phosphorus biogeochemistry, assessing ecosystem health and monitoring compliance with legislation.

Contents

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http://dx.doi.org/10.1016/j.aca.2016.02.047

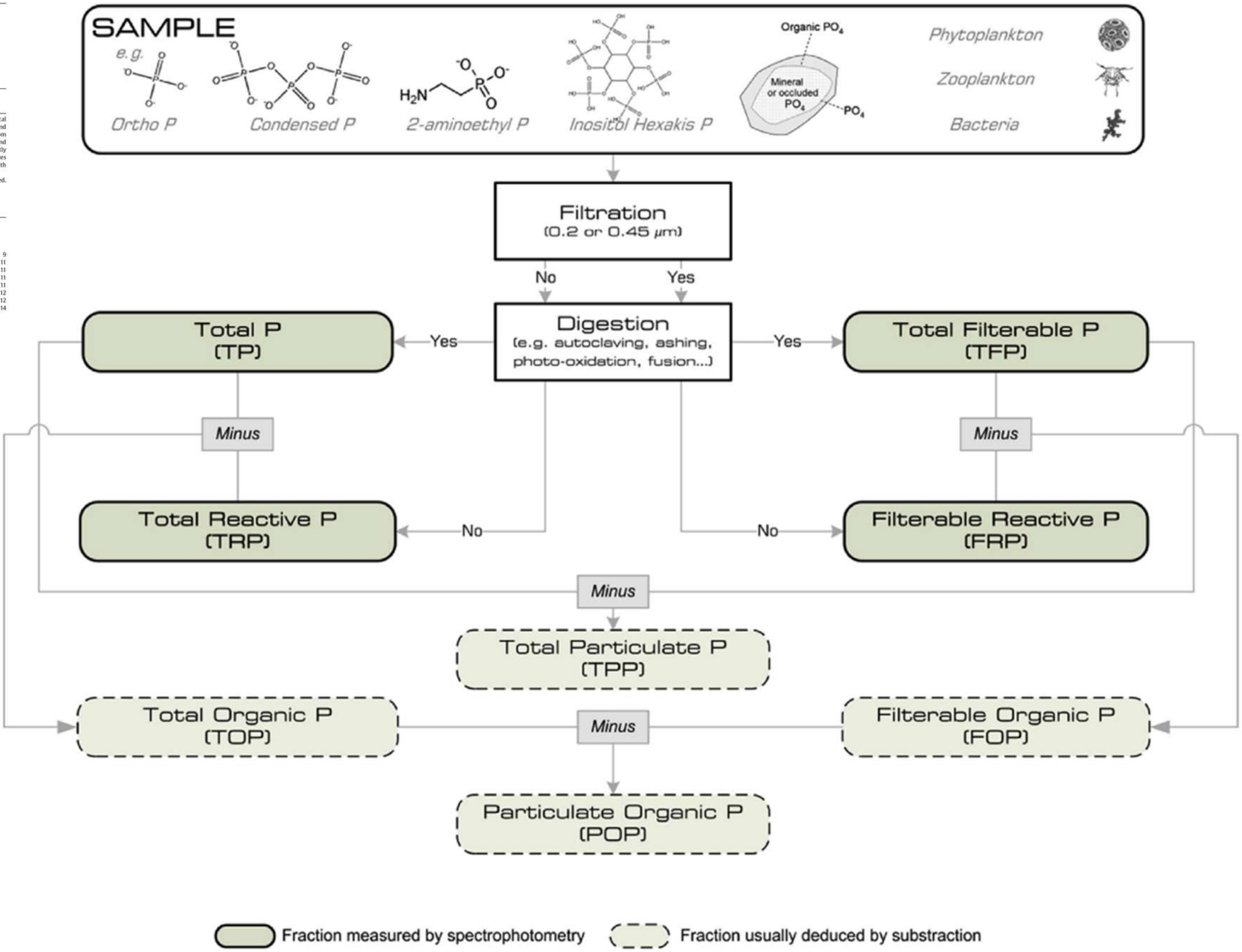
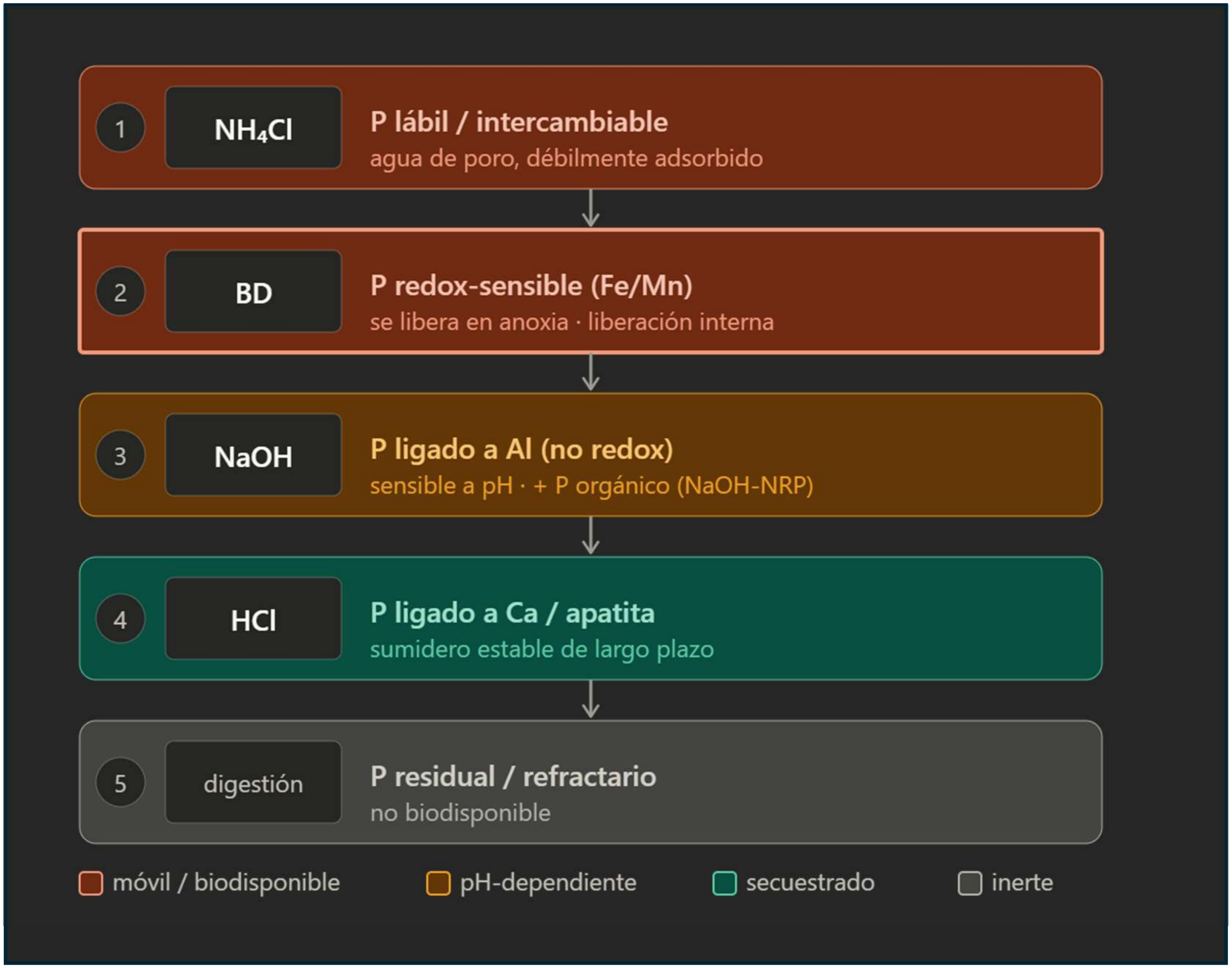


Fig. 2. The various operationally defined P fractions in natural waters, based on filtration and/or digestion.

¿en sedimentos?

Extracción secuencial de fósforo en sedimentos



1 · NH_4Cl · **P lábil / intercambiable**
agua de poro, débilmente adsorbido

↓

2 · BD · **P redox-sensible (Fe/Mn)**
se libera en anoxia · liberación interna

↓

3 · NaOH · **P ligado a Al (no redox)**
sensible a pH · + P orgánico (NaOH-NRP)

↓

4 · HCl · **P ligado a Ca / apatita**
sumidero estable de largo plazo

↓

5 · digestión · **P residual / refractario**
no biodisponible

🟥 móvil / biodisponible 🟧 pH-dependiente 🟩 secuestrado ⬜ inerte

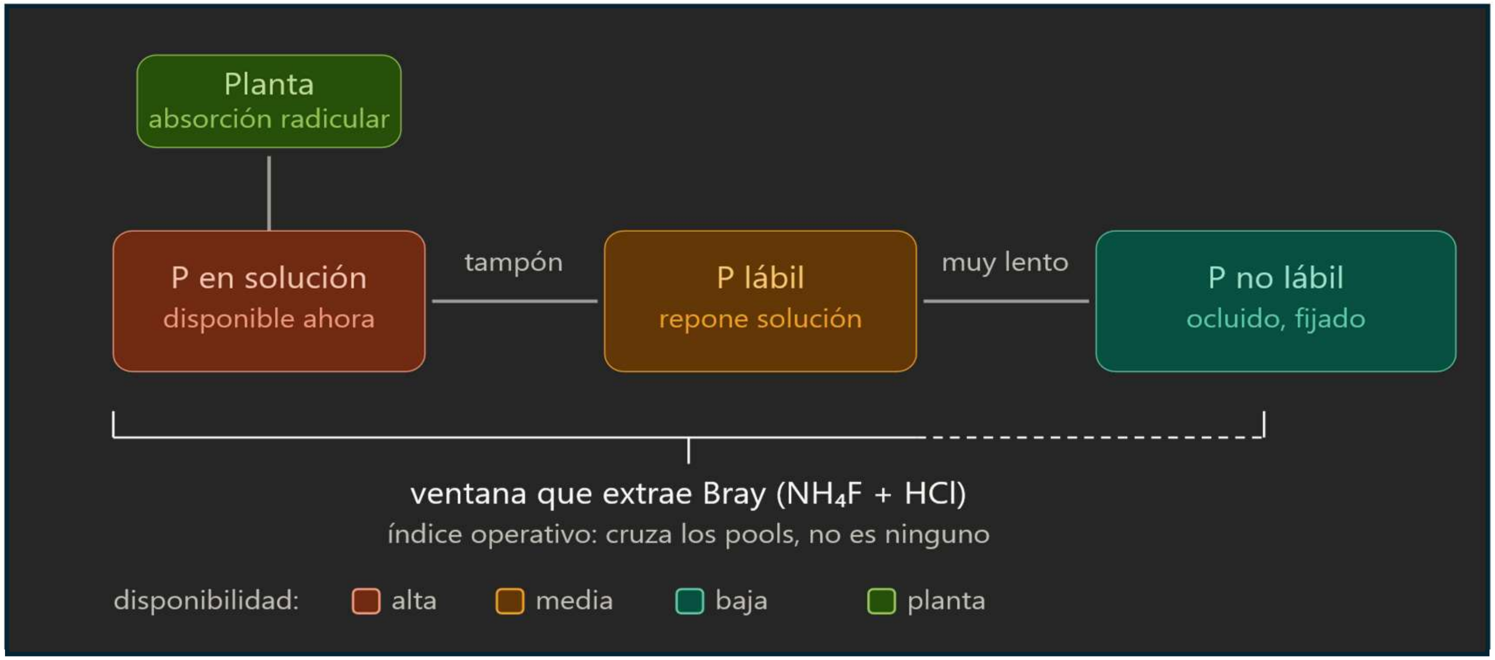
Psenner et al. 1984
(y varias modificaciones)

¿En qué unidades se expresará el resultado?

Como cantidad de fósforo por kg de sedimento seco.

¿En suelo?

Bray-1



ventana que extrae Bray (NH_4F + HCl)

índice operativo: cruza los pools, no es ninguno

Otros métodos: Mehlich, Olsen (este último preferido para pH altos)

European Journal of Soil Science, March 1998, **49**, 65–72

Forms of phosphorus transfer in hydrological pathways from soil under grazed grassland

P. M. HAYGARTH, L. HEPWORTH & S. C. JARVIS
Soil Science Group, Institute of Grassland and Environmental Research, North Wyke Research Station, Okehampton, Devon EX20 2SB, UK

Summary

Phosphorus (P) from soil can impair the water quality of streams and lakes. We have studied the forms and pathways of its movement from soil to water using 1-ha plot lysimeters, managed as grazed grassland for 12 months in temperate South-west England. The water flow through three pathways, namely (i) surface plus interflow to 30 cm (on undrained soil), (ii) surface plus interflow to 30 cm (on a mole and tile drained soil), and (iii) mole and tile drains (to 85 cm), were gauged. Samples of water from each path were treated with various combinations of 0.45-μm filtration and sulphuric acid-persulphate digestion and molybdate reaction, to determine the different forms of P. The total P (TP) concentration was greatest in the surface plus interflow to 30 cm paths (means 232 and 152 $\mu g\ l^{-1}$), whereas the mean concentration in the drainage to 85 cm was 132 $\mu g\ l^{-1}$. This reflects the substantial enrichment of the Olsen-P extracts from the surface horizons, as extracts from the 0–2 cm layer were 10-fold more than below 45 cm. In all paths, the dissolved P comprised the greatest proportion of the P transferred, with dissolved reactive P being the dominant form. Draining land reduced the transfer of TP by about 30% ($\approx 1\ kg^{-1}\ ha^{-1}\ year^{-1}$), because it can be sorbed as it flows through soil to drains. All these concentrations could cause eutrophication in surface waters.

Introduction

The average application rate of phosphorus (P) fertilizer for all grassland in England and Wales is 14 kg P ha^{-1} (Burnhill *et al.*, 1993). In addition, large quantities of P are bought into farms as feed concentrates, which find their way on to soil by excretion or as spread manures. Haygarth *et al.* (1998) have calculated that, as a result, grassland soil receives an annual P surplus (input minus output in produce) of about 24 kg P ha^{-1}. Phosphorus can become fixed in soil, which gives rise to the traditionally held opinion that it is not easily leached. This is a reasonable conclusion from an agricultural viewpoint, as transfer in leaching and runoff may represent only a small percentage of the total P in the soil. However, from a water quality perspective, where concentrations of only a few tens of $\mu g\ l^{-1}$ can cause eutrophication (Foy & Withers, 1995), this transfer of P may be significant. In view of the P surplus in grassland systems and their impact over much of the land surface of the UK (Waters, 1994), it is important to understand the processes that influence the movement from soil to water.

The forms and the pathways of P transfer need to be better understood so that land can be managed to minimize transfer. Haygarth & Jarvis (1996) have already demonstrated the magnitude of total P (TP) and dissolved reactive P (DRP) exported from grassland during storms following the application of fertilizer. There is, however, a lack in the understanding of what controls the P forms which are exported. Foy & Withers (1995) and Hawkins & Scholefield (1996) have suggested that there is much variation in the magnitude and forms of the P transferred, depending on the land from which it has originated, the transport route and the agricultural management. All of these factors interact with rainfall patterns and other environmental variables. Artificial drainage is also important because it can considerably affect the magnitude and form of P transfer (Armstrong *et al.*, 1984; Hawkins & Scholefield, 1996). Although these effects are being increasingly reported, the mechanisms involved are poorly understood. In this paper we therefore examine the effect of soil drainage on the pathways and forms of P exported from managed grassland in 1-ha grazed plot lysimeters, in relation to the variation in the soil P status with depth.

Methods

Plot lysimeter design and soil management

The Rowden drainage experiment (at North Wyke, Devon, South-west England, 7 km north of Dartmoor, British National Grid reference SX 650995) involves several nitrogen (N) and drainage treatments. It was established in 1982 on old, unimproved pasture on poorly drained sloping land (5–10%)

Correspondence: P. M. Haygarth. E-mail: haygarth@bbsrc.ac.uk
Received 24 December 1996; revised version accepted 22 July 1997

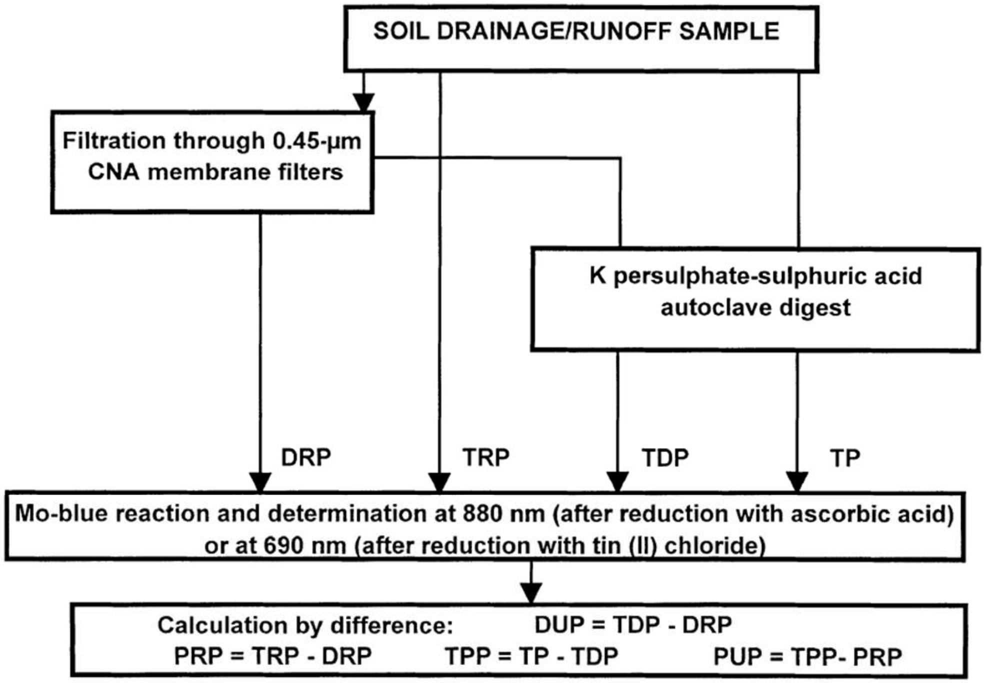


Figure 2 Operationally defined fractionation of P forms in soil waters. DRP, dissolved reactive phosphorus; TRP, total reactive phosphorus; TDP, total dissolved phosphorus; TP, total phosphorus; DUP, dissolved unreactive phosphorus; PRP, particulate reactive phosphorus; PUP, particulate unreactive phosphorus; TPP, total particulate phosphorus.

Terminology for Phosphorus Transfer

P. M. Haygarth* and A. N. Sharpley

ABSTRACT

The transfer of P from agricultural land to water attracts scientists of varied expertise. The multidisciplinary nature of factors controlling P transfer has lead to confusions in communication because of inappropriate or ambiguous use of terminology. Therefore, we have attempted to classify terminology for P transfer into: (i) *processes* (or modes) (e.g., erosion, leaching, incidental) (ii) *pathways* (e.g., overland flow, subsurface flow, drainage flow), and (iii) *form* terms (e.g., those that can be described in soil or water samples). A method of classifying pathways by scale, plane, and time is suggested and a particular caution is noted for leaching, which is a process, *not* a pathway, and runoff (a vaguely defined pathway). Current terminology for forms in water is confusing because terms such as *soluble*, *dissolved*, *particulate*, *inorganic*, and *organic* can be technically incorrect if used inappropriately when describing P forms involving membrane filtration and Murphy-Riley Mo-blue chemistry. We suggest an improved method for describing the forms of P in waters, which is operationally defined and states the analytical method and size of filter used.

IN RECENT years there has been an acceleration of fresh, estuarine, and coastal water eutrophication (Carpenter et al., 1998; Kauppi et al., 1993; Sharpley and Rekolainen, 1997). Additionally, hypereutrophic "dead zones" in the Gulf of Mexico and outbreaks of *Pfiesteria piscicida* in inland waters of the eastern USA have caused public concern and increased political pressures to identify and remediate the causative nutrient sources (Burkholder and Glasgow, 1997; Satchell, 1997; Turner and Rablalais, 1994; USEPA, 1997). In many cases, attention has focused on agriculture as a source, particularly P transfer. This is due to a decrease in the relative importance of point sources because of their ease of identification and control during the last 20 yr (Sharpley et al., 1994a). Also during this time, a specialization and intensification of agricultural systems has led to an accumulation of P in excess of crop needs in some areas (Haygarth et al., 1998a; Sharpley et al., 1998a). In response, legislation is in various stages of development and implementation to facilitate nutrient-management planning that will include P, as well as N. This has dramatically increased the need for research to provide data on which defensible P-management recommendations can be made.

In providing these data, research on P transfer from soils to waterways attracts varied and vaguely defined terminology, which ultimately causes misinterpretations and can impair scientific communication. The main reason for this is the multidisciplinary nature of the problem, as different scientific backgrounds use incompatible or ambiguous terminology. Here, we attempt to provide a simple classification of terms for P transfer based on (i) *processes* (mechanisms or modes) (ii) *pathways* (including variations in scale), and (iii) *forms*. The relevance of this classification is illustrated in Fig. 1, which shows an adaptation of the conceptual model described by Haygarth and Jarvis (1999). This model describes the P transfer regime in its entirety, and in this example we illustrate the appropriate processes, pathways, and forms.

Process Terms

Processes (mechanisms or modes) were classified by Haygarth and Jarvis (1999), who suggested that the three processes for P transfer are dissolution, incidental, and physical transfers. For example, leaching is a mechanism that would typify a dissolution process; it is commonly used and describes the elluviation of solutes through soils (Wagenet, 1990; Weaver et al., 1988a, 1988b). In fact, *leaching* is a process term that may be most appropriately applied at the micro scale, for example within the soil profile. More specific examples of mechanisms would be localized soil processes, such as mineralization, enzyme hydrolysis, or sorption/desorption.

Physical modes (macro-scale processes) are the opposite extreme to dissolution and the simplest example of these are mechanisms of detachment and soil erosion. The physical displacement and entrainment of colloids (Haygarth et al., 1997) and submicron-sized material should be included in this classification. Intermediate between dissolution and physical modes are *incidental modes* of P transfer, which describe the short-term transfer of farm amendments of P in fertilizer, manure, or animal dung. This short-term transfer of P is generally acknowledged to occur when effective rainfall removes the amendment, most often soon after application (Edwards and Daniel, 1993; Sharpley et al., 1998b; Westerman and Overcash, 1980).

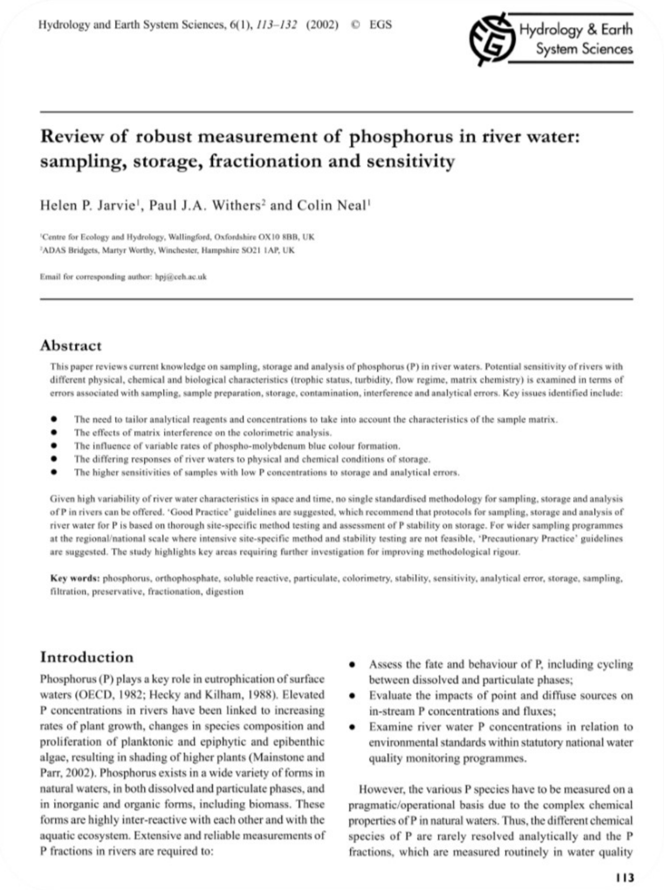
Pathway Terms

Hydrological transfer pathways are particularly difficult to classify because they incorporate a range of spatial scales of water flow, as well as variations in plane and time scale of flow. In Table 1 we have attempted to classify the most popular terms to describe pathways, which incorporates these three parameters. Other classifications of hydrochemical transfer pathways have been published, although they are of varying relevance to P transfer per se (e.g., see Anderson and Burt, 1990;

P.M. Haygarth, Institute of Grassland and Environmental Research, North Wyke Research Station, Okehampton, Devon, EX20 2SB, UK; and A.N. Sharpley, USDA-ARS, Pasture Systems and Watershed Management Research Lab., Curtin Rd., University Park, PA 16802-3702. Received 9 Sept. 1998. *Corresponding author (phil.haygarth@bbsrc.ac.uk).

Published in J. Environ. Qual. 29:10–15 (2000).

Abbreviations: DRP, dissolved reactive P; Mo, molybdate; RP, reactive P; TP, total P; unf, unfiltered; UP, unreactive P.



Hydrology and Earth System Sciences, 6(1), *113–132* (2002) © EGS

Hydrology & Earth System Sciences

Review of robust measurement of phosphorus in river water: sampling, storage, fractionation and sensitivity

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Abstract

This paper reviews current knowledge on sampling, storage and analysis of phosphorus (P) in river waters. Potential sensitivity of rivers with different physical, chemical and biological characteristics (trophic status, turbidity, flow regime, matrix chemistry) is examined in terms of errors associated with sampling, sample preparation, storage, contamination, interference and analytical errors. Key issues identified include:

- The need to tailor analytical reagents and concentrations to take into account the characteristics of the sample matrix.
- The effects of matrix interference on the colorimetric analysis.
- The influence of variable rates of phospho-molybdenum blue colour formation.
- The differing responses of river waters to physical and chemical conditions of storage.
- The higher sensitivities of samples with low P concentrations to storage and analytical errors.

Given high variability of river water characteristics in space and time, no single standardised methodology for sampling, storage and analysis of P in rivers can be offered. 'Good Practice' guidelines are suggested, which recommend that protocols for sampling, storage and analysis of river water for P is based on thorough site-specific method testing and assessment of P stability on storage. For wider sampling programmes at the regional/national scale where intensive site-specific method and stability testing are not feasible, 'Precautionary Practice' guidelines are suggested. The study highlights key areas requiring further investigation for improving methodological rigour.

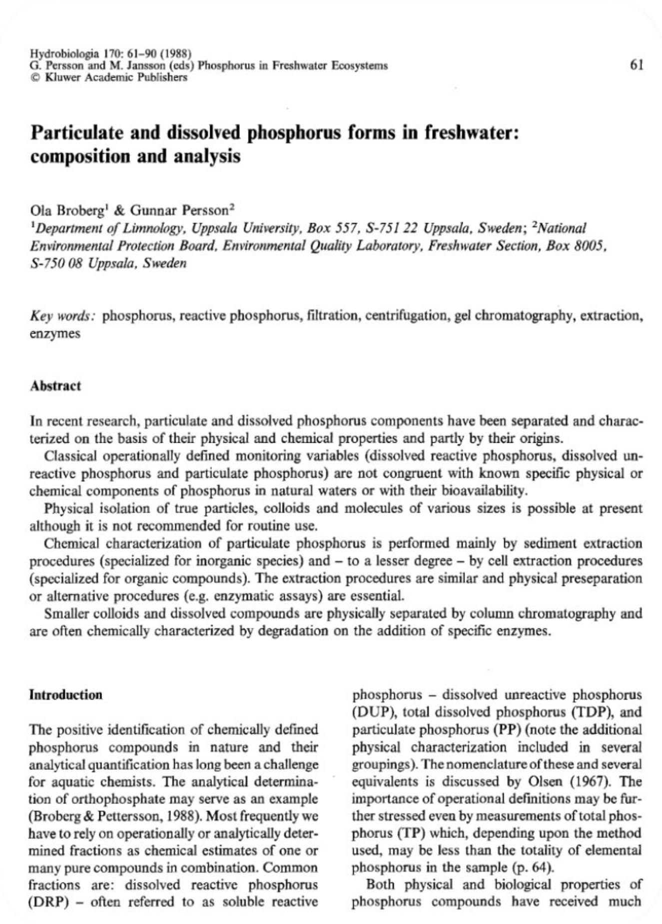
Key words: phosphorus, orthophosphate, soluble reactive, particulate, colorimetry, stability, sensitivity, analytical error, storage, sampling, filtration, preservative, fractionation, digestion

Introduction

Phosphorus (P) plays a key role in eutrophication of surface waters (OECD, 1982; Hecky and Kilham, 1988). Elevated P concentrations in rivers have been linked to increasing rates of plant growth, changes in species composition and proliferation of planktonic and epiphytic and epibenthic algae, resulting in shading of higher plants (Mainstone and Parr, 2002). Phosphorus exists in a wide variety of forms in natural waters, in both dissolved and particulate phases, and in inorganic and organic forms, including biomass. These forms are highly inter-reactive with each other and with the aquatic ecosystem. Extensive and reliable measurements of P fractions in rivers are required to:

- Assess the fate and behaviour of P, including cycling between dissolved and particulate phases;
- Evaluate the impacts of point and diffuse sources on in-stream P concentrations and fluxes;
- Examine river water P concentrations in relation to environmental standards within statutory national water quality monitoring programmes.

However, the various P species have to be measured on a pragmatic/operational basis due to the complex chemical properties of P in natural waters. Thus, the different chemical species of P are rarely resolved analytically and the P fractions, which are measured routinely in water quality



Hydrobiologia 170: 61–90 (1988)
G. Persson and M. Jansson (eds) Phosphorus in Freshwater Ecosystems
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Particulate and dissolved phosphorus forms in freshwater: composition and analysis

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Abstract

In recent research, particulate and dissolved phosphorus components have been separated and characterized on the basis of their physical and chemical properties and partly by their origins.

Classical operationally defined monitoring variables (dissolved reactive phosphorus, dissolved unreactive phosphorus and particulate phosphorus) are not congruent with known specific physical or chemical components of phosphorus in natural waters or with their bioavailability.

Physical isolation of true particles, colloids and molecules of various sizes is possible at present although it is not recommended for routine use.

Chemical characterization of particulate phosphorus is performed mainly by sediment extraction procedures (specialized for inorganic species) and – to a lesser degree – by cell extraction procedures (specialized for organic compounds). The extraction procedures are similar and physical preseparation or alternative procedures (e.g. enzymatic assays) are essential.

Smaller colloids and dissolved compounds are physically separated by column chromatography and are often chemically characterized by degradation on the addition of specific enzymes.

Introduction

The positive identification of chemically defined phosphorus compounds in nature and their analytical quantification has long been a challenge for aquatic chemists. The analytical determination of orthophosphate may serve as an example (Broberg & Pettersson, 1988). Most frequently we have to rely on operationally or analytically determined fractions as chemical estimates of one or many pure compounds in combination. Common fractions are: dissolved reactive phosphorus (DRP) – often referred to as soluble reactive phosphorus – dissolved unreactive phosphorus (DUP), total dissolved phosphorus (TDP), and particulate phosphorus (PP) (note the additional physical characterization included in several groupings). The nomenclature of these and several equivalents is discussed by Olsen (1967). The importance of operational definitions may be further stressed even by measurements of total phosphorus (TP) which, depending upon the method used, may be less than the totality of elemental phosphorus in the sample (p. 64).

Both physical and biological properties of phosphorus compounds have received much

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