

Comité Operativo Ampliado

Norma Primaria de Calidad del Aire para Compuestos Orgánicos Volátiles (COVs)

2da sesión - 16 de noviembre 2021



Tabla de la reunión

1. Bienvenida a los nuevos integrantes
2. Revisión de calendario de sesiones (5 minutos)
3. Presentación 1: Identificación de los COVs y sus riesgos en salud
Expositor: Andrés Henríquez, experto nacional, (30 minutos)
4. Presentación 2: Sistemas de monitoreo para COVs
Expositor: Felipe Reyes, Centro Mario Molina (20 minutos)
5. Preguntas y respuestas respecto a presentaciones (20 minutos)
6. Respuesta a comentarios – 1ra sesión



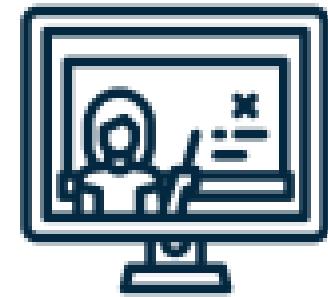
Calendario sesiones

Fechas	Temas a Desarrollar
26 de Octubre de 2021	Primer sesión - Constitución
16 de Noviembre de 2021	Segunda sesión - Presentaciones Técnicas
22 de noviembre de 2021	Tercera sesión - Presentaciones Técnicas: Normativa internacional
9 de diciembre de 2021	Cuarta sesión - Presentaciones de integrantes del COA - Plan de participación Consulta pública

Presentación 1



Identificación de los COVs y sus riesgos en salud
Expositor: Andrés Henríquez, experto nacional, (30 minutos)



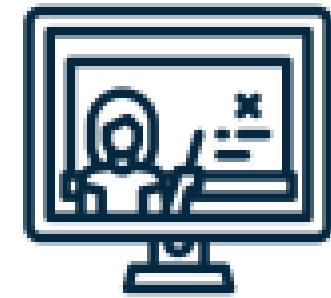
Modera: Karen Lavoz, Jefa del Departamento de Ciudadanía

Presentación 2



Sistemas de monitoreo para COVs

Expositor: Felipe Reyes, Centro Mario Molina (20 minutos)



Modera: Karen Lavoz, Jefa del Departamento de Ciudadanía

Respuesta a comentarios – 1ra sesión

- Recomendación de integrantes al COA
 - Colegio Médico
 - Municipios
 - Académico Waldo Quiroz
- Grabación de las sesiones
- Comentarios del acta anterior
 - Carolina Gómez, representante del Ministerio de Energía
 - Rubén Guzmán, representante del Ministerio de Energía
 - Nielz Cortés, representante del CRAS de Quintero - Puchuncaví

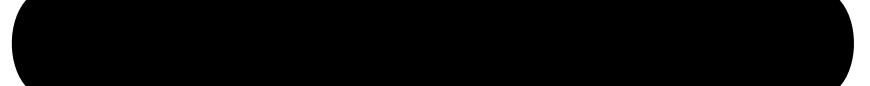




VOCs

(Volatile Organic Compounds)

Andrés Henríquez

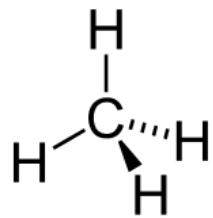


VOCs (Volatile Organic Compounds)

Volatile organic compounds (VOC) are **organic chemicals** that have a **high vapour pressure** at room temperature. High vapor pressure correlates with a **low boiling point**, which relates to the number of the sample's molecules in the surrounding air, a trait known as **volatility**

VOCs. organic and high evaporation rate

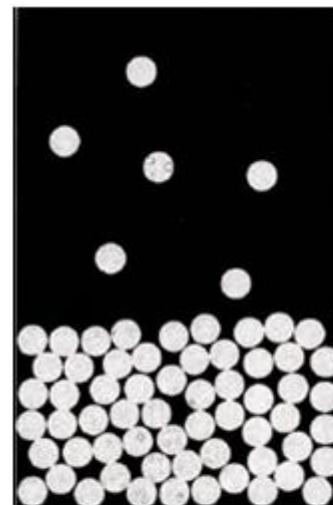
Carbon-hydrogen
bonds



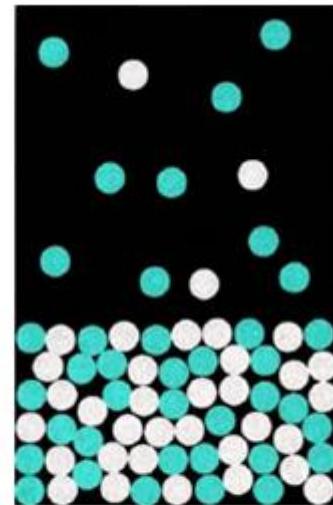
Diverse group of chemicals grouped
only due to these two properties

**Do these properties determine common
health effects after human exposure?**

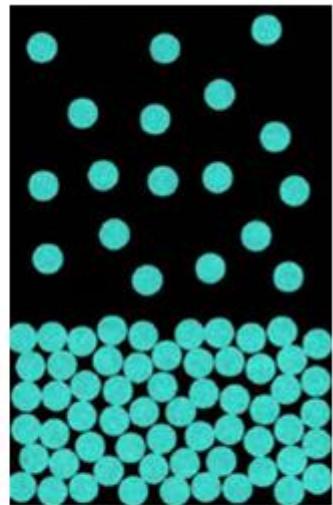
Tendency of particles to escape from the liquid (or a solid)



Vapor-liquid equilibria
for pure toluene



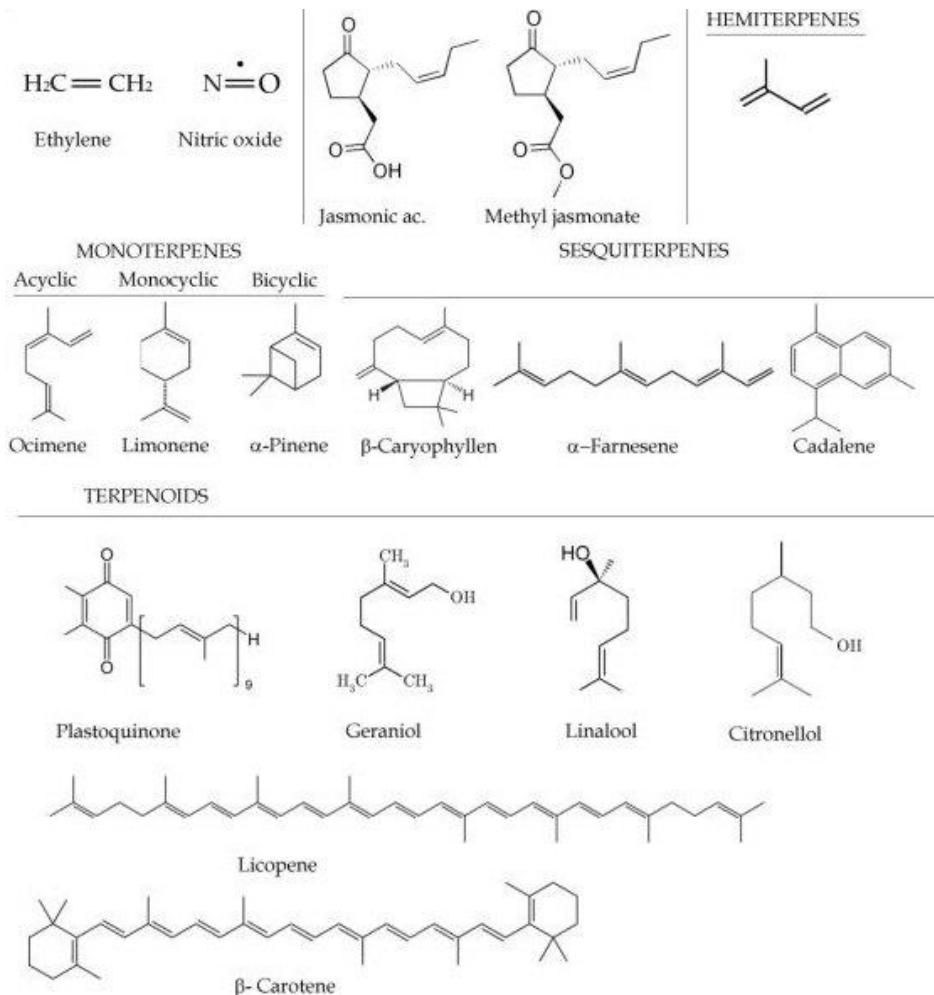
Vapor-liquid equilibria
for equal amounts of
pure toluene + benzene



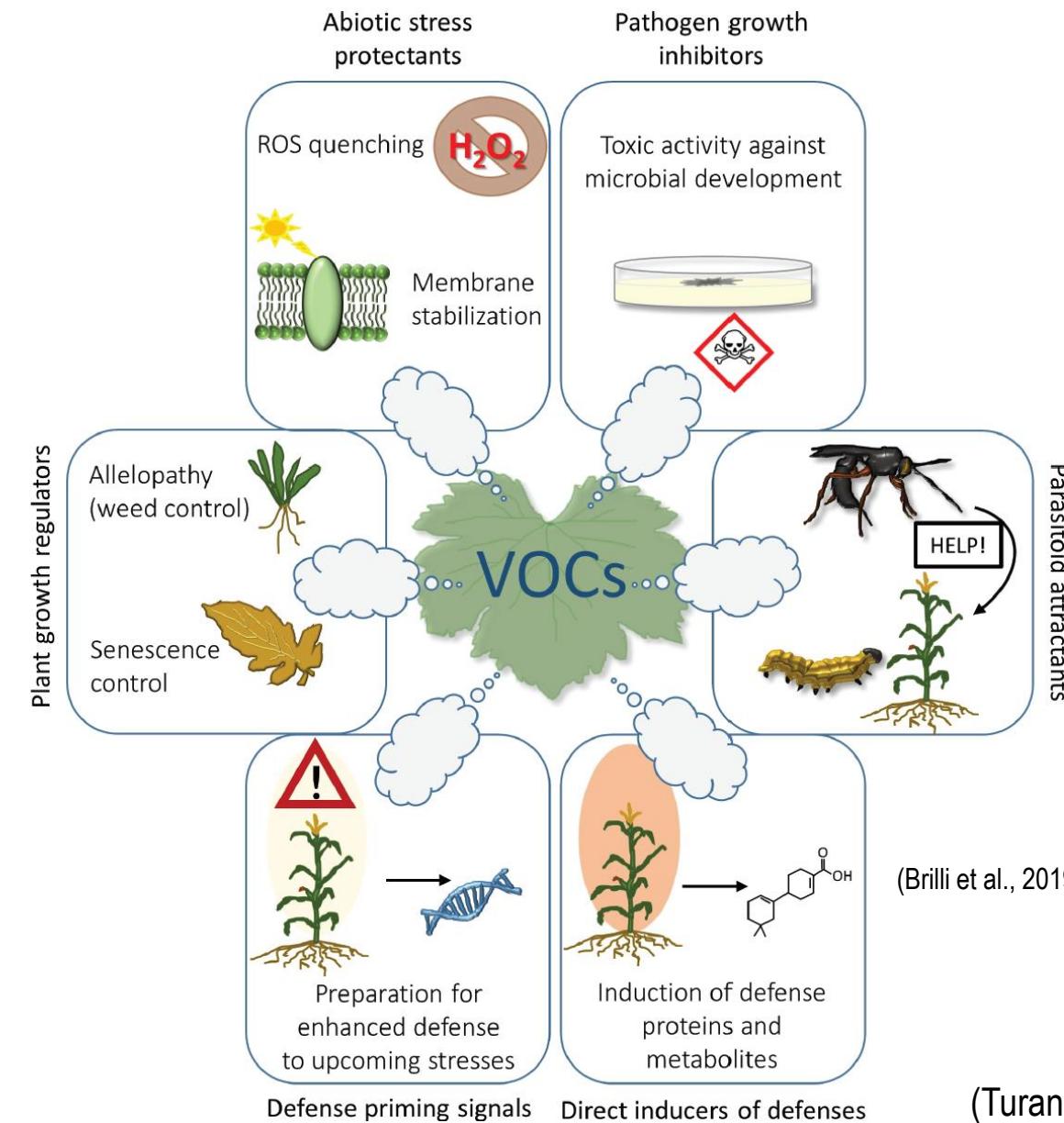
Vapor-liquid equilibria
for pure benzene

VOCs (Volatile Organic Compounds)

Biogenic (some)



<https://www.intechopen.com/books/abiotic-stress-in-plants-mechanisms-and-adaptations/emission-and-function-of-volatile-organic-compounds-in-response-to-abiotic-stress>



VOCs (Volatile Organic Compounds)

001162

https://sor.epa.gov/sor_internet/registry/substreg/searchandretrieve/advancedsearch/search.do?details=displayDetails&selectedSubstanceId=83723

“Although a **large number of substances are considered VOCs**, the most abundant in the environment are **benzene** and some of its organic derivatives, like **toluene, ethylbenzene and xylene (o-, m- and p-)**, jointly named BTEX, which comprise over **60% of the VOCs found in urban areas [8]**; hence, **they are used as a reference to evaluate environmental levels and VOC exposure.**“

(Montero-Montoya et al., 2018)

VOCs (Volatile Organic Compounds)

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BTEX

Benzene
Toluene
Ethylbenzene
Xylene (o,m,p)

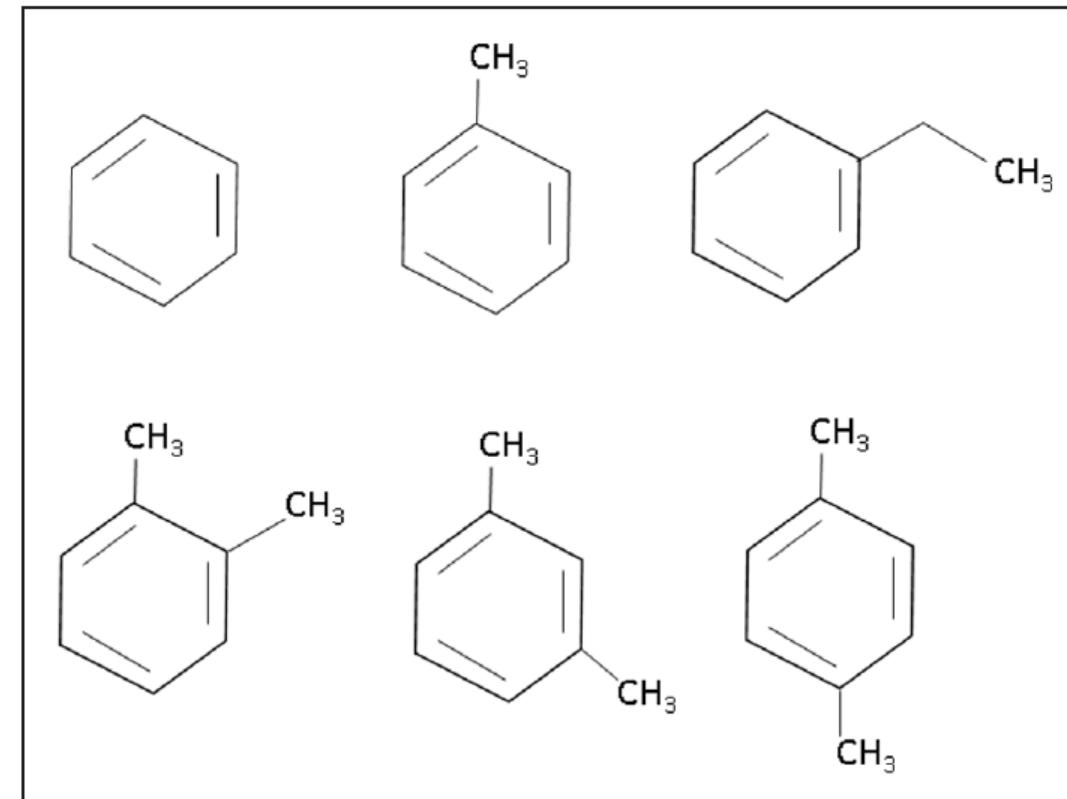


Figure 2: Chemical structure of BTEX. Upper line: benzene, toluene and ethylbenzene. Lower line: orto-, meta- and para-xylene.

Montero-Montoya
et al. 2018

BTEX (RfC and Cancer)

IRIS: U.S. EPA. Integrated Risk Information System (IRIS)

RfC: An estimate (with uncertainty spanning perhaps a factor of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.

		Benzene	Toluene	Ethylbenzene	Xylenes			
RfC	30 ug/m ³	Decreased lymphocyte count	5000 ug/m ³	Neurological effects in occupationally-exposed workers	1000 ug/m ³	Developmental toxicity	100 ug/m ³	Impaired motor coordination (decreased rotarod performance)
Cancer assessment characterization	WOE	Known/likely human carcinogen	Inadequate information to assess carcinogenic potential	D (Not classifiable as to human carcinogenicity)	Data are inadequate for an assessment of human carcinogenic potential			
		Quantitative Estimate of Carcinogenic Risk from Inhalation Exposure (PDF) (45 pp, 261 K). Inhalation Unit Risk: 2.2×10^{-6} per $\mu\text{g}/\text{m}^3$. Extrapolation Method: Low-dose linearity utilizing maximum likelihood estimates Tumor site(s): Hematologic. Tumor type(s): Leukemia (Rinsky et al., 1981, 1987 Paustenbach et al., 1993 Crump and Allen, 1984 Crump, 1992, 1994 U.S. EPA, 1998)	inadequate information to assess the carcinogenic potential of toluene because studies of humans chronically exposed to toluene are inconclusive, toluene was not carcinogenic in adequate inhalation cancer bioassays of rats and mice exposed for life (CIIT, 1980 NTP, 1990 Huff, 2003),		Nonclassifiable due to lack of animal bioassays and human studies.		Adequate human data on the carcinogenicity of xylenes are not available, and the available animal data are inconclusive as to the ability of xylenes to cause a carcinogenic response. Evaluations of the genotoxic effects of xylenes have consistently given negative results.	
Framework for WOE characterization	Proposed Guidelines for Carcinogen Risk Assessment (U.S. EPA, 1996)		Guidelines for Carcinogen Risk Assessment (U.S. EPA, 2005)	Guidelines for Carcinogen Risk Assessment (U.S. EPA, 1986)	Revised Draft Guidelines for Carcinogen Risk Assessment (U.S. EPA, 1999)			

Benzene: Routes of exposure

“Inhalation accounts for more than **99%** of the exposure of the general population, whereas **intake from food and water is minimal”**

(WHO, 2000)

Table I. Personal Exposures to Benzene Compared to Ambient Levels in Five TEAM Study Locations

Location	No. of Samples		Concentration ^a	
	Personal	Outdoor	Personal	Outdoor
NJ	340	86	28	9
MD	70	70	19	8
L.A.	232	132	14	8
A-P	68	10	8	2
NC	24	6	9	3
Total	734	304	16	6

^a Population-weighted 24-hour arithmetic mean ($\mu\text{g}/\text{m}^3$): NJ = Bayonne-Elizabeth, New Jersey (Fall 1981); MD = Baltimore, Maryland (Spring 1987); L.A. = Los Angeles, California (two seasons, 1984 and 1987); A-P = Antioch-Pittsburgh, California (June 1984); NC = Greensboro, North Carolina (May 1982).

Personal and indoor exposure to benzene is substantial

(Wallace, 1989)

Benzene: Routes of exposure

Inhalation accounts for more than **99%** of the exposure of the general population, whereas **intake from food and water is minimal**

(WHO, 2000)

Indoor exposure to benzene is substantial, probably driven by cigarette smoke.

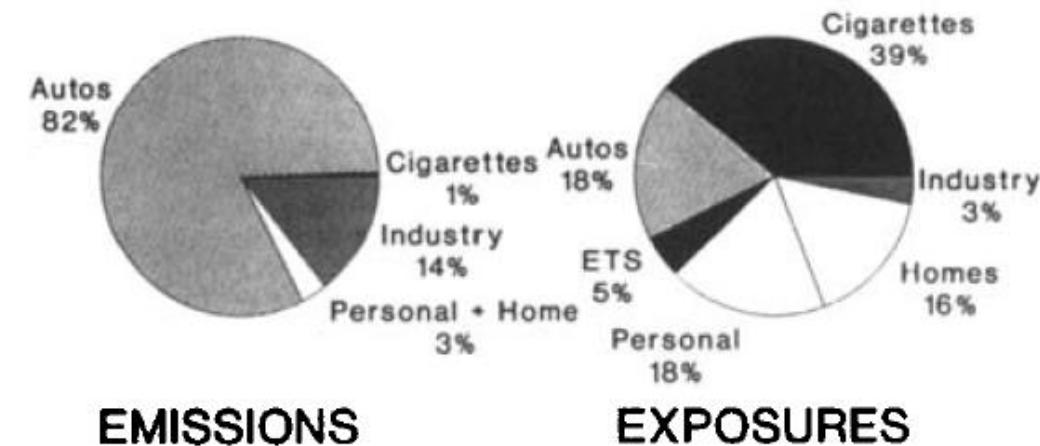


Fig. 1. Benzene: Emissions vs. exposures (TEAM study, Los Angeles, 1987).

(Wallace, 1989)

Benzene: Risk Assessment

Pliofilm Study



Just before the war, when Pliofilm was made available for commercial purposes, it became evident that Pliofilm was likely to revolutionise the whole field of packing materials. For Pliofilm proved to be water-proof, water moisture vapour-proof, dust-proof, acid-proof, germ-proof and oil-proof. Naturally, then, the impact of this amazing product upon industry and commerce was enormous. But war came — and at once the entire production of Pliofilm was turned over to war industry. Today, even aircraft engines arrive here packed in Pliofilm.

Pliofilm is a result of that ceaseless research and development which forever goes on in the Goodyear organisation. The vast array of problems which Pliofilm is solving today will remain to bestow themselves upon industry and commerce when peace comes round. ★ (PLIOFILM — a registered trade mark of the Goodyear Tire & Rubber Co.).

Another
GOOD YEAR
contribution to progress

Rubber and Benzene



Benzene: Risk Assessment

Leukemia Risk Associated with Benzene Exposure in the Pliofilm Cohort

Mary Burr Paxton

American Petroleum Institute, Washington, DC

1996

Pliofilm Study

Table 3. Lymphatic and hematopoietic cancers in the Pliofilm cohort.

Case no.	Plant location	First benzene exposure	Last benzene exposure	Year of death	Age at death	ICD ^a code	Cause of death
<i>In old cohort^b</i>							
1	St. Marys	1940	1942	1958	36	204.2	Monocytic leukemia
2	St. Marys	1948	1948	1950	29	204.1	Chronic myelogenous leukemia
3	Akron	1945	1958	1958	60	204.3	Acute myelocytic leukemia
4	Akron	1944	1958	1960	65	204.3	Acute myelogenous leukemia
5	Akron	1939	1960	1961	62	204.3	DiGuglielmo's acute myelocytic leukemia
6	Akron	1941	1961	1961	57	204.3	Acute granulocytic leukemia
7	Akron	1942	1948	1957	57	204.2	Acute monocytic leukemia
8	St. Marys	1950	1952	1954	28	204.1	Myelogenous leukemia
9	Akron	1942	1960	1979	67	205.0	Acute myeloblastic leukemia
10 ^c	St. Marys	1954	1954	1980	69	203	Multiple myeloma
11 ^c	St. Marys	1940	1940	1963	52	203	Multiple myeloma
12 ^c	St. Marys	1943	1968	1968	62	203	Plasma cell sarcoma
13 ^c	St. Marys	1954	1955	1981	68	203	Multiple myeloma
14 ^d	St. Marys	1937	1970	1973	64	200.0	Reticulosarcoma
15 ^d	St. Marys	1947	1955	1978	55	202.9	Other malignant neoplasm of lymphoid or histiocytic tissue
<i>Added in update</i>							
16	Akron	1950	1957	1984	67	205.1	Chronic myeloid leukemia
17	Akron	1948	1958	1985	67	205.0	Acute myeloid leukemia
18	St. Marys	1940	1956	1985	67	204.0	Acute lymphoid leukemia
19	St. Marys	1945	1946	1986	71	208.9	Unspecified leukemia
20	St. Marys	1949	1949	1987	81	208.9	Unspecified leukemia
21 ^e	Akron	1943	1945	1974	82	205.0	Acute myeloid leukemia
22 ^d	Akron	1947	1947	1987	61	202.8	Other lymphoma

^aInternational Classification of Diseases code currently on 1987 update of NIOSH tape. ^bRinsky et al. (4). ^cThe four cases with ICD Code of 203 (multiple myeloma and immunoproliferative neoplasms) were not considered in further analyses. ^dThe three cases of hematopoietic/lymphatic cancers other than leukemia, multiple myeloma, or plasma cell sarcoma were not considered in further analyses. ^eThis one female leukemia case was not considered in the SMR analyses but was included in the dose-response analysis using the proportional hazards model.

Pliofilm Study

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Tabla 5: Riesgo de desarrollar leucemia debido a inhalación de benceno según diferentes evaluaciones para el estudio de los trabajadores de pliofilm.

+

Riesgos estimados calculados en base al estudio de trabajadores de Pliofilm por diferentes investigadores.

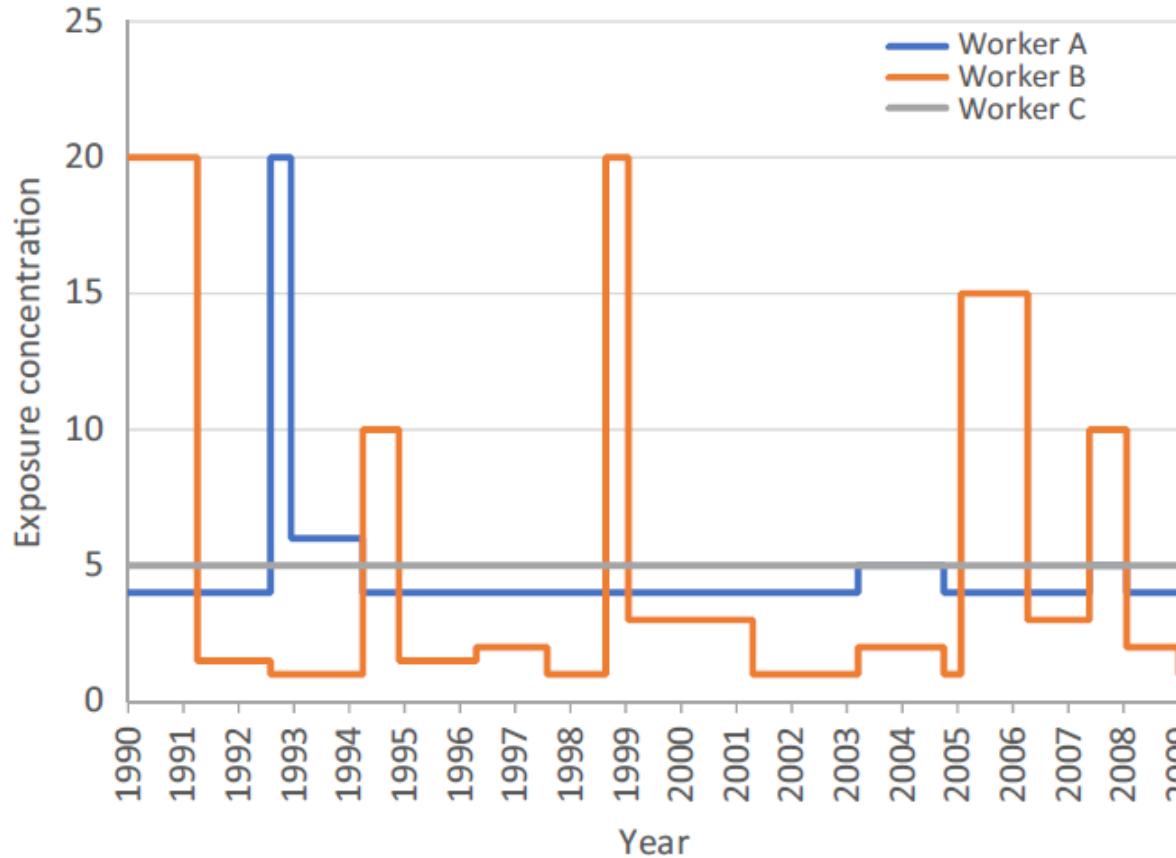
Fuente	Riesgo a 1ppm (3.19 mg/m ³)	Riesgo a 1ppb (3.19 µg/m ³)	Modelo de exposición
US EPA (1985)	1.8E-2 (7.5E-3, 3.4E-2)	1.8E-5 (7.5E-6, 3.4E-5)	Crump and Allen, additive risk
	4.1E-2 (1.3E-3, 8.8E-2)	4.1E-5 (1.3E-5, 8.8E-5)	Crump and Allen, relative risk
Brett et al. 1989	4.03E-3 (1.0E-3, 1.2E-2) a 2.5E-2 (2.5E-3, 9.9E-2)	3.6E-6 (9.5E-7, 6.9E-6) a 1.1E-5 (2.2E-6, 1.9E-5)	Crump and Allen, conditional logistic
	2.2E-1 (1.2E-2, 1.0) a 8.4E-1 (1.5E-2, 1.0)	2.4E-5 (6.9E-6, 4.2E-5) a 3.4E-5 (8.2E-6, 5.9E-5)	Rinsky, conditional logistic
Paxton 1992	2.2E-3 (3.8E-5, 4.9E-3)	1.9E-6 (3.7E-8, 3.7E-6)	Crump and Allen, proportional hazard
	4.6E-3 (1.3E-3, 9.0E-3)	3.5E-6 (1.2E-6, 5.8E-6)	Paustenbach, proportional hazard
Crump 1992, 1994	1.8E-2 (3.0E-3, 5.5E-2)	8.9E-6 (2.5E-6, 1.5E-5)	Rinsky, proportional hazard
	1.1E-2 (2.2E-3, 2.0E-2) a 2.5E-2 (6.03E-3, 1.3E-1)	1.1E-5 (2.2E-56 2.0E-5) a 2.5E-5 (6.03E-6, 1.3E-4)	Crump and Allen, linear
Crump 1992, 1994	5.4E-3 a 2.5E-2	4.5E-6 a 2.6E-5	Crump and Allen, nonlinear
	7.1E-3 (2.0E-3, 1.2E-2) a 1.5E-2 (3.8E-3, 2.6E-2)	7.2E-6 (2.0E-6, 1.2E-5) a 1.6E-25 (3.8E-6, 2.6E-5)	Paustenbach, linear
	8.6E-5 a 6.5E-3	8.6E-11 a 5.65E-6	Paustenbach, nonlinear

Tabla adaptada desde "Carcinogenic Effects of Benzene: An Update", (EPA, 1998)

analyses and
re-analyses



Assumptions regarding exposure



Difficulties

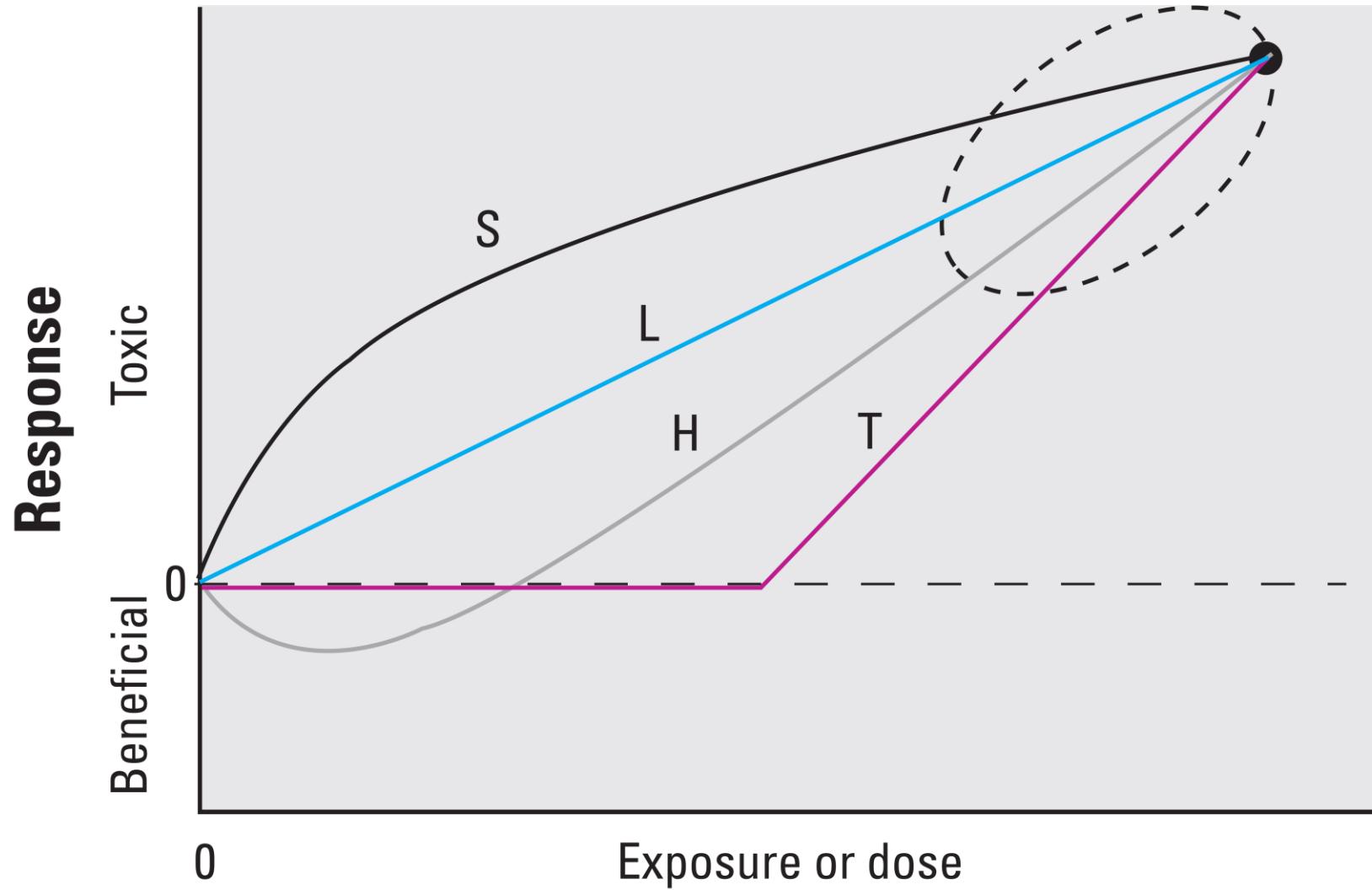
Fig. 1. Peak exposure profiles for three workers with identical cumulative exposure after 20 years. Worker A encounters one peak, Worker B encounters five peaks, and Worker C does not encounter peaks.

(Checkoway et al., 2019)

Carcinogenic Effects of Benzene: An Update

US EPA. 1998

“Currently, there is insufficient evidence to deviate from using an assumption of a linear response curve for benzene, hence, the Agency’s past approach of using a model with low-dose linearity is still recommended”



Benzene: Risk Assessments

001167

EPA	WHO	UE
Rango		Rango
2.23E-06	7.84E-06	5.88E-06

Estimaciones del efecto a la exposición al benceno, expuestos como el riesgo de desarrollar leucemia durante el transcurso de la vida debido a la exposición a 1 µg/m³ de benceno.

2.23 – 7.84 casos de leucemia por millón de habitantes debido a la exposición a 1 µg/m³ (durante el periodo de vida promedio)

INCERTEZA

Smoking and subsequent risk of acute myeloid leukaemia: A pooled analysis of 9 cohort studies in Japan

“One of the most likely mechanisms of the leukaemogenic effect of smoking leads is **through benzene**. Benzene is a **an established risk factor for AML**, and an association between exposure to high levels of benzene and an increased risk of AML has been reported”

(Ugai et al., 2018)

Benzene Metabolism

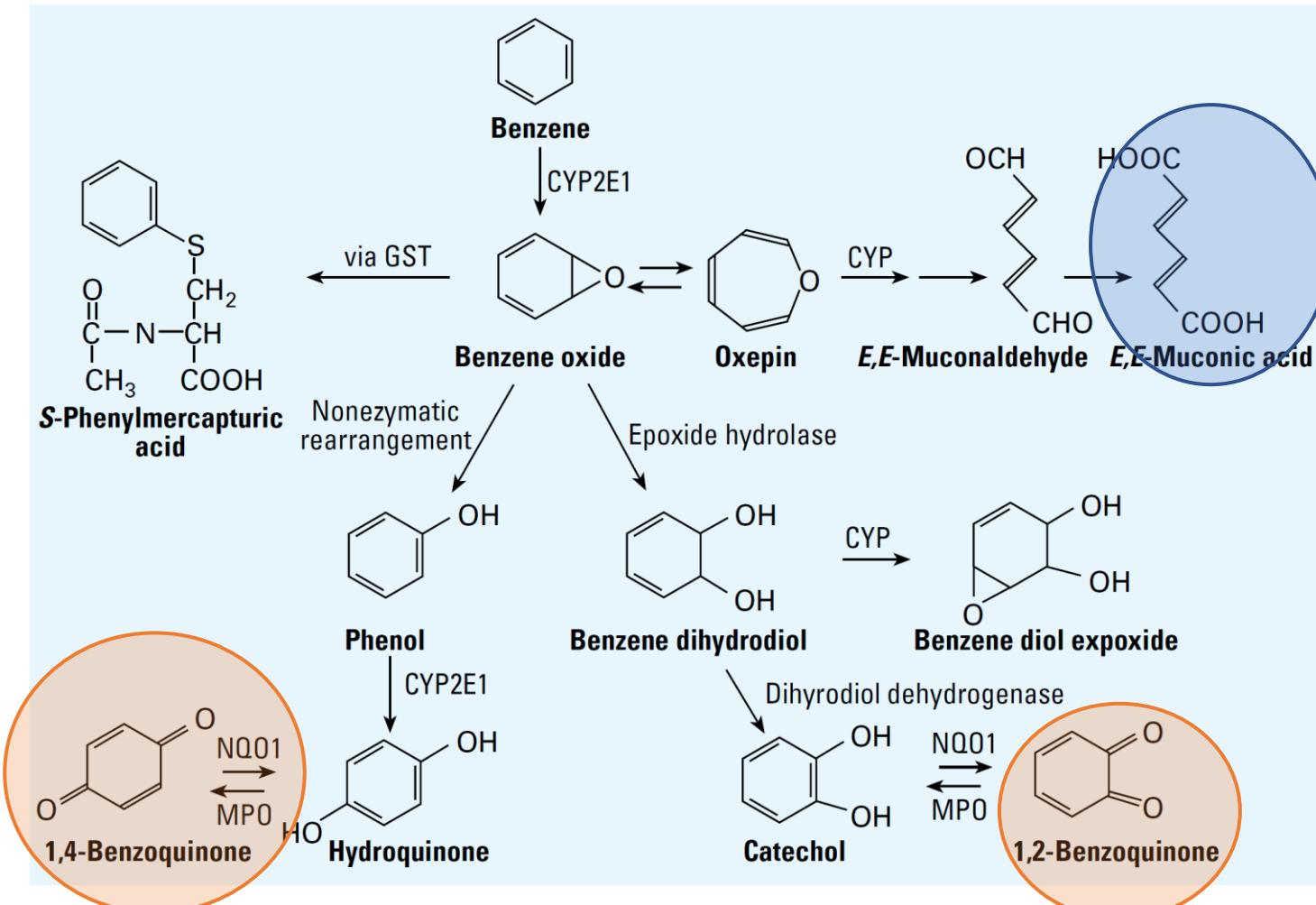


Figura 1: Esquema metabólico para el benceno mostrando las vías más importantes y las enzimas (genes) mediando la transformación de metabolitos. GST (glutathione-S-transferase), NQO1 (NAD(P)H:quinone oxidoreductase 1), MPO (myeloperoxidase), CYP2E1 (cytochrome P450 2E1). Figura obtenida desde Rappaport et al. 2009.

Exposure biomarker

Benzoquinones:
reactive
compounds

Benzene Metabolism (location, location, location)^{001168 vta}

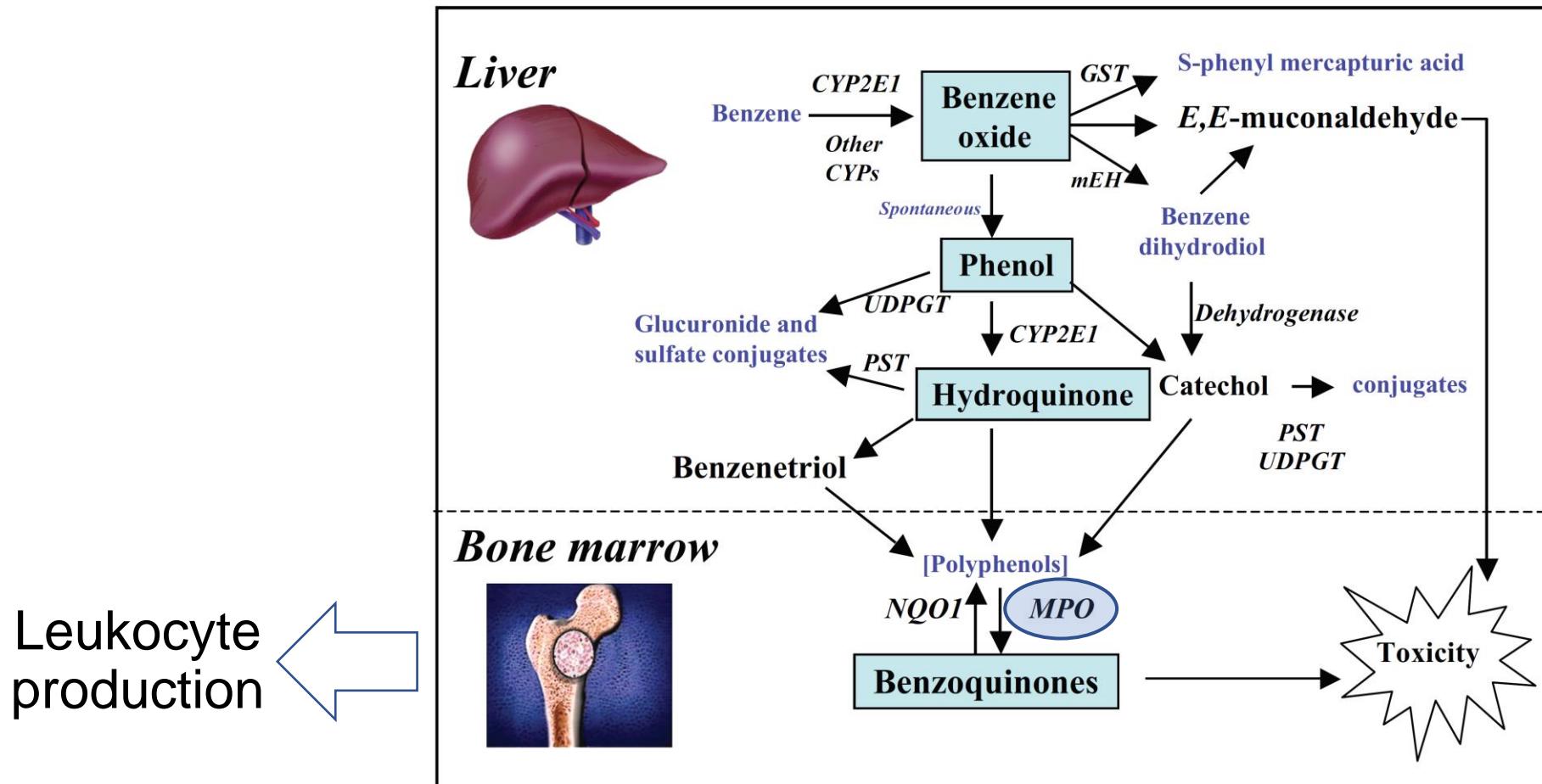


Figura 1: Esquema metabólico para el benceno que produce toxicidad. GST (glutathione-S-transferase), NQO1 (NAD(P)H:quinone oxidoreductase 1), MPO (myeloperoxidase), CYP2E1 (cytochrome P450 2E1), UDPGT (uridine diphosphate glucuronyl transferase), PST (phenol sulfotransferase), mEH (microsomal epoxide hydrolase). Figura obtenida desde Martyn T. Smith, 2010.

BTEX (RfC and Cancer)

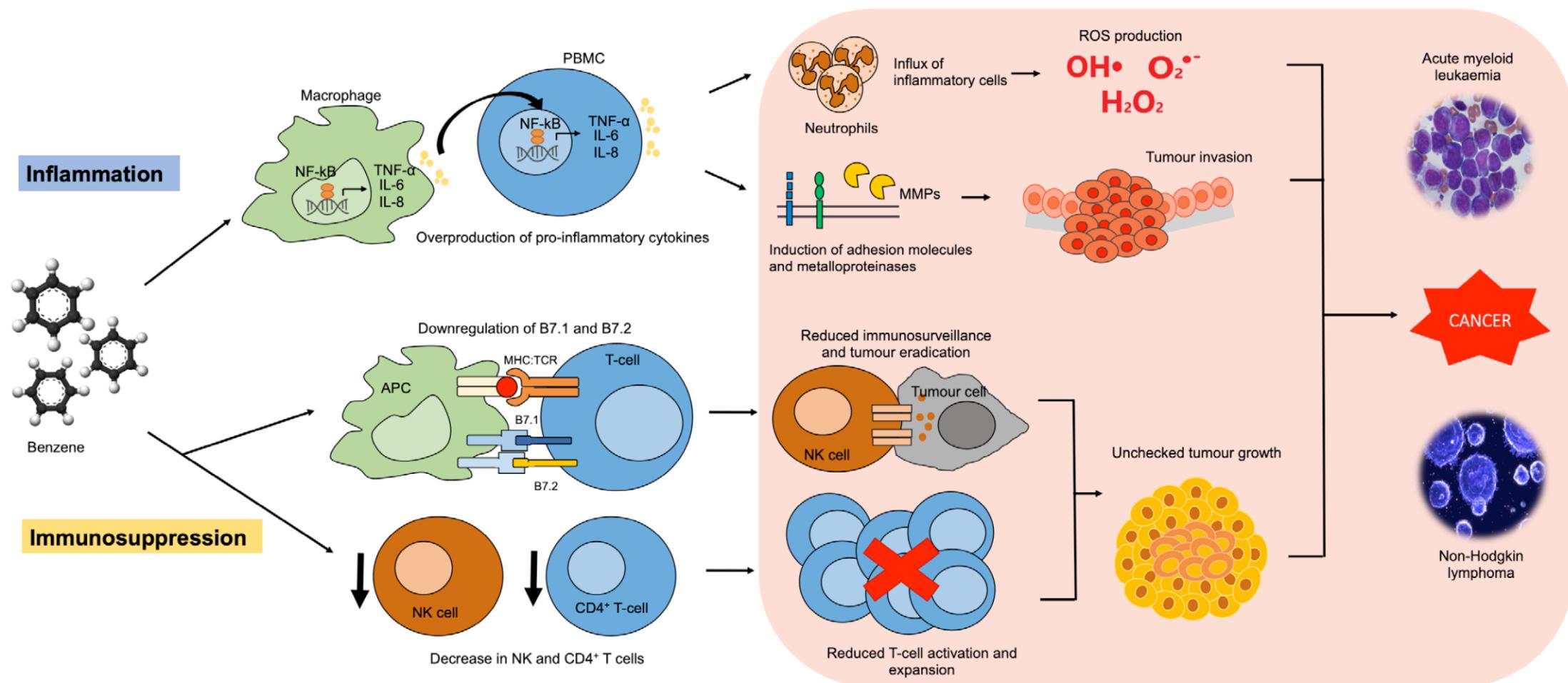
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Framework for WOE characterization	Proposed Guidelines for Carcinogen Risk Assessment (U.S. EPA, 1996)		Guidelines for Carcinogen Risk Assessment (U.S. EPA, 2005)	Guidelines for Carcinogen Risk Assessment (U.S. EPA, 1986)	Revised Draft Guidelines for Carcinogen Risk Assessment (U.S. EPA, 1999)			

Other mechanisms: Chronic Inflammation

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Abbreviations: APC, antigen-presenting cell; NK, natural killer; MMPs, matrix metalloproteinases, PBMC, peripheral blood mononuclear cell; ROS, reactive oxygen species

Figure 2 Proposed mechanism of benzene-facilitated carcinogenesis via chronic inflammation and immunosuppression.

Guo et al. 2020

Different mechanisms have been reported

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Identification and categorization process

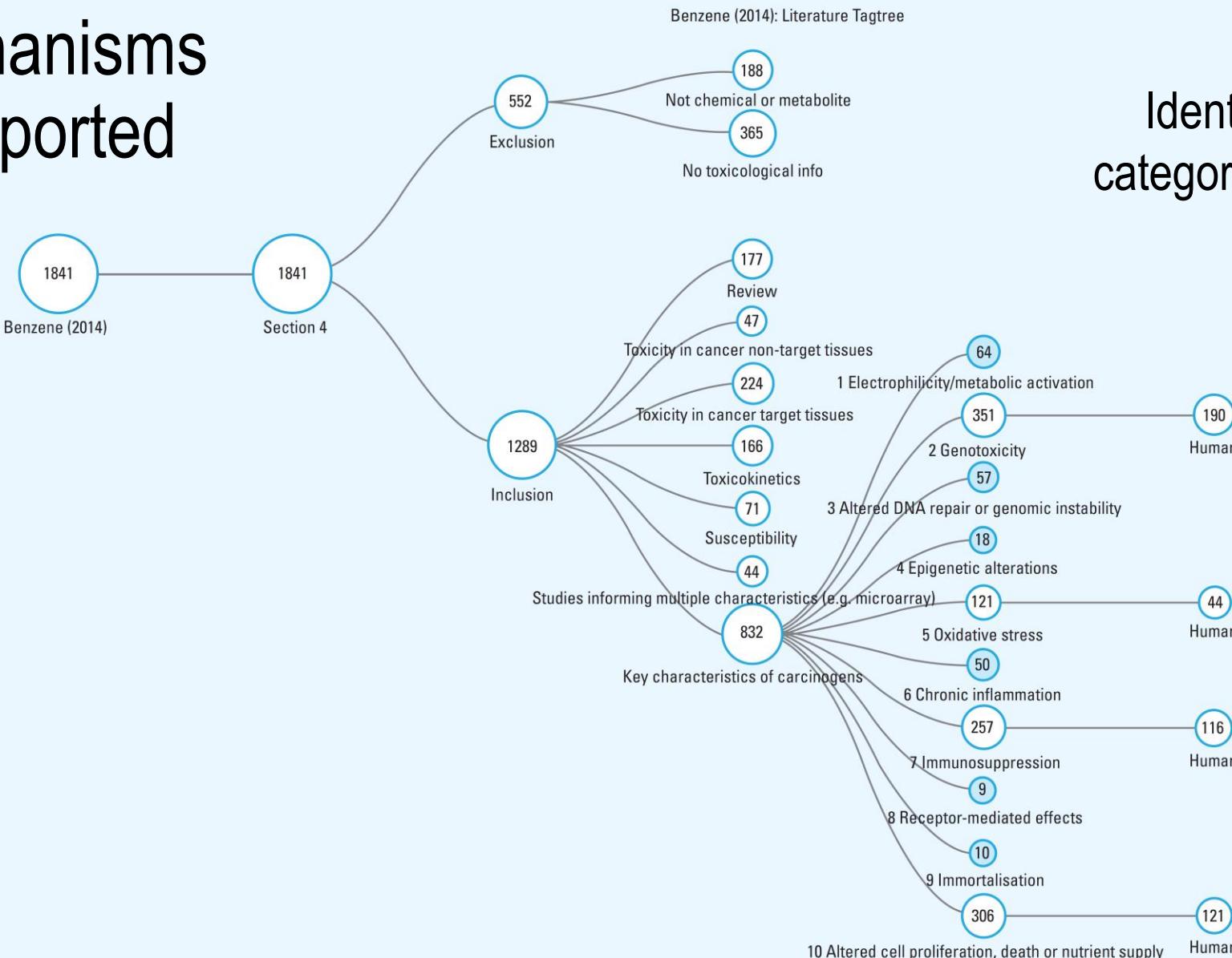


Figure 1. Literature flow diagram, illustrating the systematic identification and categorization process for benzene mechanistic studies. Using appropriate MeSH terms and key words, targeted literature searches were conducted for the 10 key characteristics using online tools available from the HAWC Project (<https://hawcproject.org/>). Section 4 refers to the location of the discussion of mechanistic data within the IARC Monograph structure (<http://monographs.iarc.fr/ENG/Preamble/currentb4studiesother0706.php>). All inclusion categories were expanded to document the number of studies attributed to each, down to the individual key characteristic level, which were expanded to illustrate human information when > 100 total studies were identified. Less frequently encountered key characteristic categories (blue-shaded circles) were left unexpanded for clarity. "Human" refers to both humans exposed *in vivo* and human cells exposed *in vitro*.

Smith et al., 2016

EXAMPLES

Verification of the effect on risk^{001170 vta}
to reduction of benzene discharge

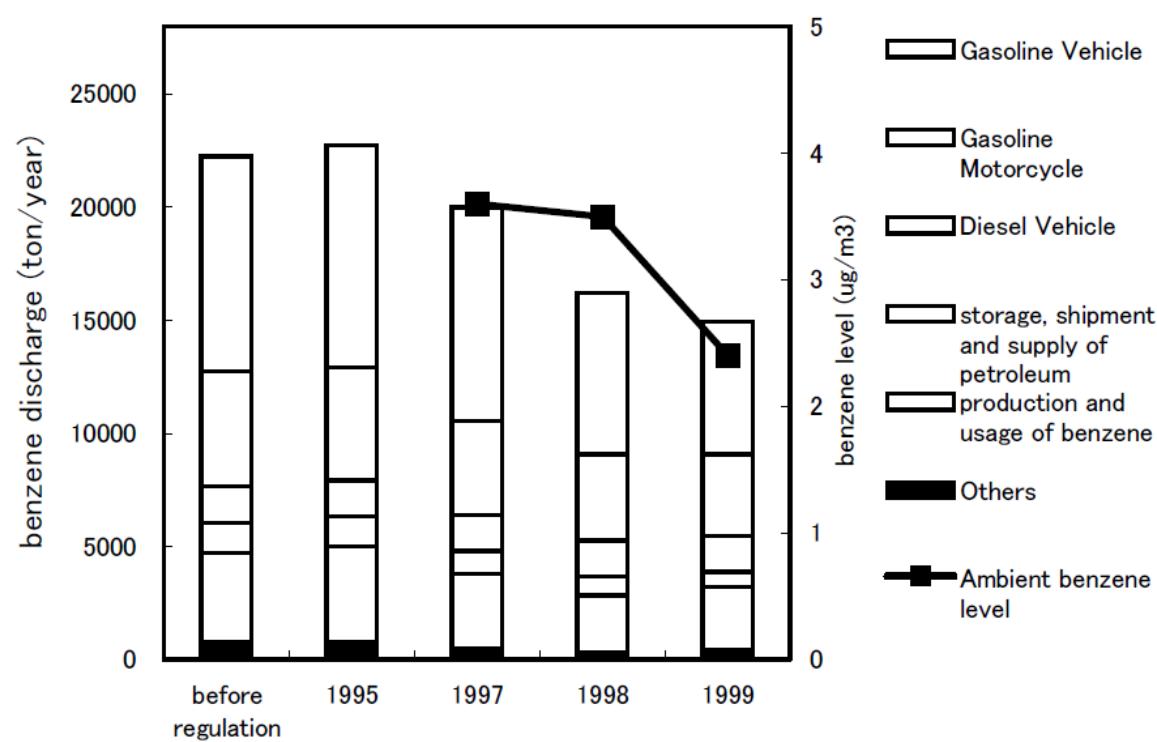


Fig. 3 Comparison of time course of benzene discharge and ambient benzene level in Japan in the 1990s.

Hideo Kajihara ^{a,*}, Akihiro Fushimi ^b, Junko Nakanishi ^{b,c}

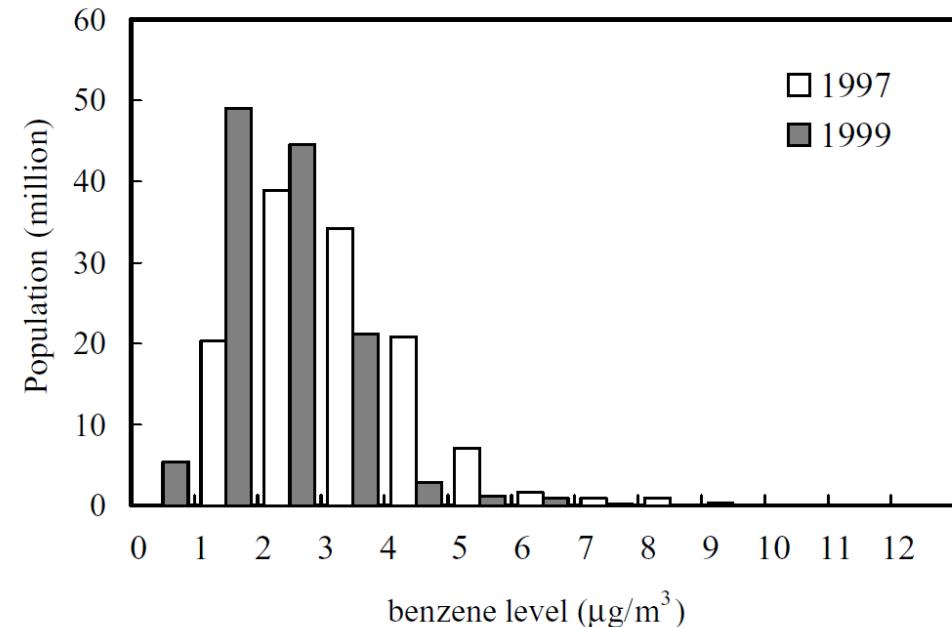


Fig. 5. Change of histograms representing the relationship between the ambient benzene level and the Japanese population living there.

"The change of the ambient benzene level was well explained by the change of the discharge data. Risk reduction due to the reduction of benzene discharge was estimated to be 17 cases per year."

(Kajihara et al., 2003)

EXAMPLES

One-year measurements of toxic benzene concentrations in the ambient air of Greece: An estimation of public health risk



Paraskevi Begou*, Pavlos Kassomenos

Laboratory of Meteorology, Department of Physics, University of Ioannina, GR-45110, Ioannina, Greece

Table
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Pati
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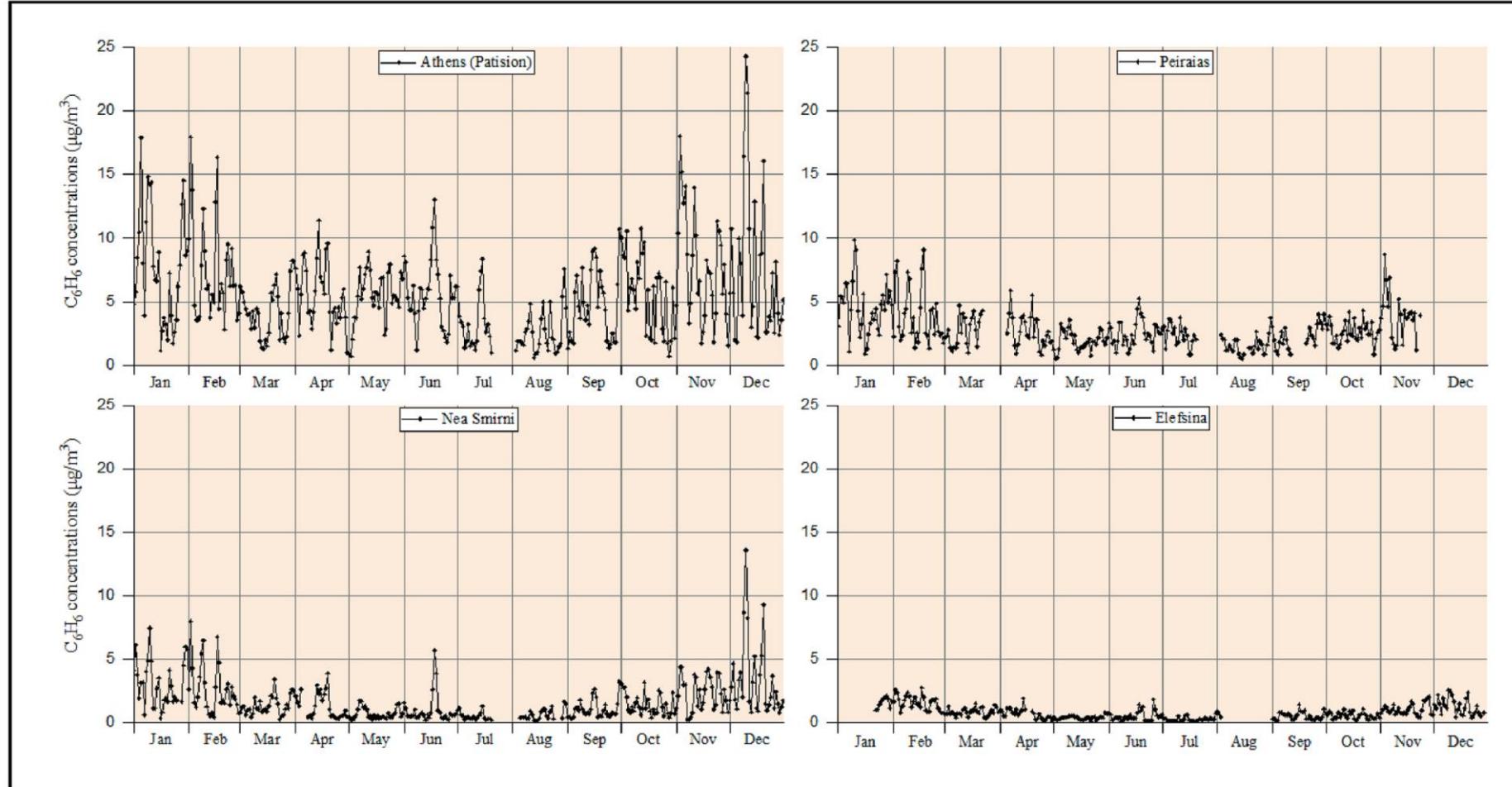


Fig. 2. Daily variations of the benzene concentrations at the air quality monitoring stations in the GAA, during the year 2016.

xamined air quality mon-

Nov	Dec
1.96E-06	1.85E-06
9.92E-07	8.43E-07
5.98E-07	3.44E-07
2.72E-07	1.52E-06
7.71E-07	1.09E-06
9.18E-07	4.84E-07

(Begou &
Kassomenos, 2020)

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Because the observed health impacts associated with the various pollutants occur over different exposure times.					
	Pollutant	Concentration	Averaging period	Legal nature	Permitted exceedences each year
Fine particles (PM2.5)	25 µg/m ³ ***	1 year		Target value to be met as of 1.1.2010 Limit value to be met as of 1.1.2015	n/a
Sulphur dioxide (SO ₂)	350 µg/m ³	1 hour		Limit value to be met as of 1.1.2005	24
Nitrogen dioxide (NO ₂)	125 µg/m ³	24 hours		Limit value to be met as of 1.1.2005	3
PM10	200 µg/m ³	1 hour		Limit value to be met as of 1.1.2010	18
	40 µg/m ³	1 year		Limit value to be met as of 1.1.2010 *	n/a
	50 µg/m ³	24 hours		Limit value to be met as of 1.1.2005 **	35
	40 µg/m ³	1 year		Limit value to be met as of 1.1.2005 **	n/a
Lead (Pb)	0.5 µg/m ³	1 year		Limit value to be met as of 1.1.2005 (or 1.1.2010 in the immediate vicinity of specific, notified industrial sources; and a 1.0 µg/m ³ limit value applied from 1.1.2005 to 31.12.2009)	n/a
Carbon monoxide (CO)	10 mg/m ³	Maximum daily 8 hour mean		Limit value to be met as of 1.1.2005	n/a
Benzene	5 µg/m ³	1 year		Limit value to be met as of 1.1.2010**	n/a
Ozone	120 µg/m ³	Maximum daily 8 hour mean		Target value to be met as of 1.1.2010	25 days averaged over 3 years
Arsenic (As)	6 ng/m ³	1 year		Target value to be met as of 31.12.2012	n/a
Cadmium (Cd)	5 ng/m ³	1 year		Target value to be met as of 31.12.2012	n/a
Nickel (Ni)	20 ng/m ³	1 year		Target value to be met as of 31.12.2012	n/a
Polycyclic Aromatic Hydrocarbons	1 ng/m ³ (expressed as concentration of Benzo(a)pyrene)	1 year		Target value to be met as of 31.12.2012	n/a

*Under Directive 2008/50/EU the Member State could apply for an extension of up to five years

Table 3. Health Effects of Ambient Exposure to Benzene^a

health outcome	N	exposure concn	effect size (OR; 95% CI) ^b	citation
development				
biparietal diameter	81	$\geq 2.6 \mu\text{g}/\text{m}^3$	(−1.3; −2.6 to −0.1) ^c	Slama et al. ⁸⁵
birth weight	1601703	1.975–4.929 $\mu\text{g}/\text{m}^3$	(1.82; 1.64–2.02) ^c	Zahran et al. ⁸⁷
		<1.4 to $\geq 2.6 \mu\text{g}/\text{m}^3$	(−68; −135 to −1) ^c	Slama et al. ⁸⁵
	270	1.6 $\mu\text{g}/\text{m}^3$	(16.2; −24.6 to 56.9)	Estarlich et al. ⁸⁶
	2337	1.1 ppbV	(1.03; 1.00 to 1.05) ^d	Ghosh et al. ⁸⁸
low birth weight	354688			
head circumference	85	$\geq 2.6 \mu\text{g}/\text{m}^3$	(−3.7; −7.3 to 0.0) ^c	Slama et al. ⁸⁵
	2337	1.6 $\mu\text{g}/\text{m}^3$	(0.04; −0.09 to 0.17)	Estarlich et al. ⁸⁶
preterm birth	785	>2.7 $\mu\text{g}/\text{m}^3$	(6.46; 1.58 to 26.35) ^c	Llop et al. ⁸⁴
spina bifida	4531	>2.86–7.44 $\mu\text{g}/\text{m}^3$	(1.77; 1.04 to 3.00) ^c	Lupo et al. ⁸³
immune function				
atopy	1629	per 1 $\mu\text{g}/\text{m}^3$ increase	(0.98; 0.88 to 1.09)	Hirsch et al. ^{92,g}
	86	6.32–12.59 $\mu\text{g}/\text{m}^3$	$\beta = 0.32^e$	Choi et al. ⁹³
alveolar macrophages	321	6.4 mg/L	(1.32; 1.1 to 2.32) ^c	Dutta et al. ⁹⁵
CD4+/CD25+ t-cells	56	3.3 $\mu\text{g}/\text{m}^3$	(−0.92; 1.00 to 1.81) ^d	Baiz et al. ³⁴
dysplasia	321	6.4 mg/L	(1.71; 1.26 to 4.22) ^c	Dutta et al. ⁹⁵
eczema				
	321	2.41 $\mu\text{g}/\text{m}^3$	(1.48; 1.24–1.75) ^c	Zhou et al. ⁹⁰
in last year				
	15 to 3.3 $\mu\text{g}/\text{m}^3$	(1.11; 1.0 to 1.28) ^d	Penard-Morand et al. ⁹¹	
eosinophils	321	6.4 mg/L	(1.75; 1.19 to 4.22) ^c	Dutta et al. ⁹⁵
IL-3 eosinophil/basophils	40	dnr	$r = 0.432^e$	Junge et al. ⁹⁷
IL-5 eosinophil/basophils	40	dnr	$r = 0.371^e$	Junge et al. ⁹⁷
lymphocytes	321	6.4 mg/L	(1.45; 1.21 to 3.44) ^c	Dutta et al. ⁹⁵
metaplasia	321	6.4 mg/L	(1.67; 1.22 to 5.45) ^c	Dutta et al. ⁹⁵
miR-223	316	1.01 $\mu\text{g}/\text{m}^3$	(1.17; 1.07 to 1.29) ^c	Herberth et al. ⁹⁶
MLH1	140	7.96 mg/L	(1.44; 1.02 to 2.10) ^c	Mukherjee et al. ⁹⁴
MSH2	140	7.96 mg/L	(1.64; 1.04 to 2.36) ^c	Mukherjee et al. ⁹⁴
neutrophils	321	6.4 mg/L	(1.22; 1.05 to 3.19) ^c	Dutta et al. ⁹⁵
sensitization to pollen	4907	1.5–3.3 $\mu\text{g}/\text{m}^3$	(1.24; 1.0–1.52) ^d	Penard-Morand et al. ⁹¹
WBC count	20	369 $\mu\text{g}/(\text{g of Cr})$	$r = -0.51^e$	Pelallo-Martinez et al. ⁹⁸
metabolic function				
HOMA-IR (insulin resistance)	505	0.032 mg/(g of Cr)	(2.00; 1.16–3.46) ^{c,f}	Choi et al. ¹¹³
reproductive function				
asthenospermic	32	170–430 ng/mL	(nES) ^c	Ducci et al. ⁸⁹
normospermic	32	170–430 ng/mL	(nES) ^c	Ducci et al. ⁸⁹
oligospermic	32	170–430 ng/mL	(nES) ^c	Ducci et al. ⁸⁹
teratospermic	32	170–430 ng/mL	(nES) ^c	Ducci et al. ⁸⁹
sperm concn	32	170–430 ng/mL	$r = -0.62^e$	Ducci et al. ⁸⁹
% normal sperm	32	170–430 ng/mL	$r = -0.41^e$	Ducci et al. ⁸⁹
% viable sperm	32	170–430 ng/mL	$r = -0.89^e$	Ducci et al. ⁸⁹
respiratory function				
asthma	192	per 10 $\mu\text{g}/\text{m}^3$ increase	(2.922; 2.25–3.795) ^c	Rumchev et al. ⁹⁹
		n/a	(4.95; 0.91–27.4)	Rive et al. ¹⁰⁵
	111	0.3–53.5 $\mu\text{g}/\text{m}^3$	(1.3; 0.4–3.8)	Hulin et al. ¹⁰⁶
in the last year	1012	2.0 $\mu\text{g}/\text{m}^3$	(1.43; −0.65 to 4.75)	Billionne et al. ¹⁰⁷
lifetime	4907	1.5–3.3 $\mu\text{g}/\text{m}^3$	(1.36; 1.0–1.96) ^d	Penard-Morand et al. ⁹¹
	4907	1.5–3.3 $\mu\text{g}/\text{m}^3$	(1.25; 1.08–1.43) ^c	Penard-Morand et al. ⁹¹
exercise-induced	2104	1.50–6.95 $\mu\text{g}/\text{m}^3$	(0.72; 0.48–1.07)	Bentayeb et al. ¹⁰⁸
	4907	1.5–3.3 $\mu\text{g}/\text{m}^3$	(1.32; 1.03–1.82) ^c	Penard-Morand et al. ⁹¹
	1228	3–9 ppb	(1.28; 0.76–2.13)	Gordian et al. ¹⁰²
current	1039	>9 ppb	(1.48; 0.81–2.73)	Gordian et al. ¹⁰²
current ^c	3233	4.74 to >7.27 $\mu\text{g}/\text{m}^3$	(2.045; 1.227–3.407) ^c	Nicolai et al. ¹⁰⁰
physician-diagnosed	1255	4.74 to >7.27 $\mu\text{g}/\text{m}^3$	(2.047; 1.235–4.692) ^c	Nicolai et al. ¹⁰⁰
	550	1.21 $\mu\text{g}/\text{m}^3$	(1.33; 1.13–1.56) ^c	Arif and Shah ¹⁰¹
	1228	3–9 ppb	(1.04; 0.67–1.63)	Gordian et al. ¹⁰²
	1039	>9 ppb	(1.06; 0.61–1.85)	Gordian et al. ¹⁰²
	4209	2.41 $\mu\text{g}/\text{m}^3$	(0.97; 0.81–1.15)	Zhou et al. ⁹⁰
severe asthma	2203	per 1 $\mu\text{g}/\text{m}^3$ increase	(1.21; 1.01–1.45) ^c	Hirsch et al. ^{92,g}
	1228	3–9 ppb	(1.34; 0.70–2.54)	Gordian et al. ¹⁰²
	1039	>9 ppb	(2.49; 1.22–5.07) ^c	Gordian et al. ¹⁰²
symptoms	80	5.67 ng/L	(5.93; 1.64–21.4) ^c	Delfino et al. ¹⁰³

Acute effects of benzene exposure: development, immune function, respiratory function, metabolic function, reproductive function

(Bolden et al. 2015)

health outcome	N	exposure concn	effect size (OR; 95% CI) ^b	citation
bronchitis	74	1.82 ppb	(1.23; 1.02–1.48) ^{c,f}	Delfino et al. ¹⁰⁴
obstructive bronchitis	2114	per 1 $\mu\text{g}/\text{m}^3$ increase	(1.16; 1.04–1.29) ^c	Hirsch et al. ^{92,g}
cough	192	>3.6 $\mu\text{g}/\text{m}^3$	(10; 1.57–63.34) ^c	Rolle-Kampczyk et al. ¹¹⁶
	2211	per 1 $\mu\text{g}/\text{m}^3$ increase	(1.21; 1.04–1.40) ^c	Hirsch et al. ⁹²
EBC pH	3206	4.74 to >7.27 $\mu\text{g}/\text{m}^3$	(1.423; 1.01–2.005) ^c	Nicolai et al. ¹⁰⁰
FEV in 1 s	2104	1.50–6.95 $\mu\text{g}/\text{m}^3$	(0.78; 0.56–1.09)	Bentayeb et al. ¹⁰⁸
	51	1.0–10.7 ($\mu\text{g}/\text{m}^3$)/week ^h	(−0.24; −0.42–−0.06) ^c	Martins et al. ¹¹⁰
FEV in 1 s	51	1.0–10.7 ($\mu\text{g}/\text{m}^3$)/week ^h	(−4.33; −7.13 to −1.53) ^c	Martins et al. ¹¹⁰
FEV in 1 s, <85% predicted	72	2.80 $\mu\text{g}/\text{m}^3$	(−4.7; −18.8 to 9.5)	Smargiassi et al. ¹¹¹
FEF 25–75% of FVC	992	per 1 $\mu\text{g}/\text{m}^3$ increase	(1.17; 0.81–1.67)	Hirsch et al. ⁹²
	51	1.0–10.7 ($\mu\text{g}/\text{m}^3$)/week ^h	(−5.89; −10.16 to −1.62) ^c	Martins et al. ¹¹⁰
FEF 25–75%, <70% predicted	72	2.80 $\mu\text{g}/\text{m}^3$	(−3.5; −34.2 to 27.1)	Smargiassi et al. ¹¹¹
FEV in 1 s/FVC	981	per 1 $\mu\text{g}/\text{m}^3$ increase	(1.17; 0.92–1.50)	Hirsch et al. ⁹²
oxidative stress (8OHdG)	51	1.0–10.7 ($\mu\text{g}/\text{m}^3$)/week ^h	(−1.71; −3.24 to −0.18) ^c	Martins et al. ¹¹⁰
pulmonary infections	154	0.08 mg/L	$\beta = 8.23^e$	Yoon et al. ¹¹²
wheeze	256	>5.6 $\mu\text{g}/\text{m}^3$	(2.4; 1.3–4.5) ^c	Diez et al. ¹⁰⁹
	3192	4.74 to >7.27 $\mu\text{g}/\text{m}^3$	(1.646; 1.062–2.552) ^c	Nicolai et al. ¹⁰⁰
	2218	per 1 $\mu\text{g}/\text{m}^3$ increase	(1.08; 0.90–1.29)	Hirsch et al. ⁹²
	6634	3.57 $\mu\text{g}/\text{m}^3$	(1.08; 1.02–1.13) ^c	Buchdahl et al. ¹¹⁷
other physiological effects	4209	2.41 $\mu\text{g}/\text{m}^3$	(0.99; 0.84–1.15)	Zhou et al. ⁹⁰
hematocrit	20	369 $\mu\text{g}/(\text{g of Cr})$	$r = -0.64^e$	Pelallo-Martinez et al. ⁹⁸
hemoglobin	20	369 $\mu\text{g}/(\text{g of Cr})$	$r = -0.60^e$	Pelallo-Martinez et al. ⁹⁸
RBC count	20	369 $\mu\text{g}/(\text{g of Cr})$	$r = -0.42^e$	Pelallo-Martinez et al. ⁹⁸



LABOR LAETITIA NOSTRA



Investigación & desarrollo

A I R F L U X

MÉTODOS DE MONITOREO COVs y REGULACIÓN INTERNACIONAL

2da sesión del Comité operativo ampliado del proceso de
elaboración de la Norma primaria de calidad del aire para COVs

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████████████████████@cmmolina.cl

Martes 16 de Noviembre 2021
Santiago, Chile

ALCANCE

PPDA CQP

A partir de los resultados de los monitoreos realizados, el Ministerio del Medio Ambiente iniciará, en el plazo de 18 meses contado desde la publicación del presente decreto, la **elaboración de una norma primaria de calidad del aire referida a contaminantes clasificados como COVs**, que puedan presentar impactos en la salud por la calidad del aire.

Ley de Bases del Medio Ambiente Norma Primaria de Calidad Ambiental:

- Establece los valores de las concentraciones y períodos, máximos o mínimos permisibles
- **riesgo para la vida** o la salud de la población.
- **Aplicación general en todo el territorio de la República**
- Define los niveles que originan situaciones de emergencia.

ESQUEMA

ALCANCE NORMATIVO INTERNACIONAL

SISTEMAS DE MONITOREO DE COVs PARA
PROPOSITOS REGULATORIOS

ALCANCE NORMATIVO INTERNACIONAL

COV: DOS ENFOQUES DIFERENTES

	USEPA	UE
Efectos en la salud	<p>Enfoque Intradomiciliario “Contaminantes Peligrosos del Aire” US EPA risk assessment guidelines (2005)</p>	<p>Extradomiciliario Norma de calidad de Benceno (5 ug/m³)</p>
Rol en la formación de O ₃		<p>Enfoque Extradomiciliario NO_x, COV</p>

COMPUESTOS ORGÁNICOS VOLÁTILES...

Aunque una gran cantidad de sustancias se consideran COV, las más abundantes en el medio ambiente son el **benceno** y sus derivados (**ETX**), que comprenden más de 60 % de los COV encontrados en áreas urbanas; por lo tanto, se utilizan como referencia para evaluar los niveles ambientales y la exposición a COV".

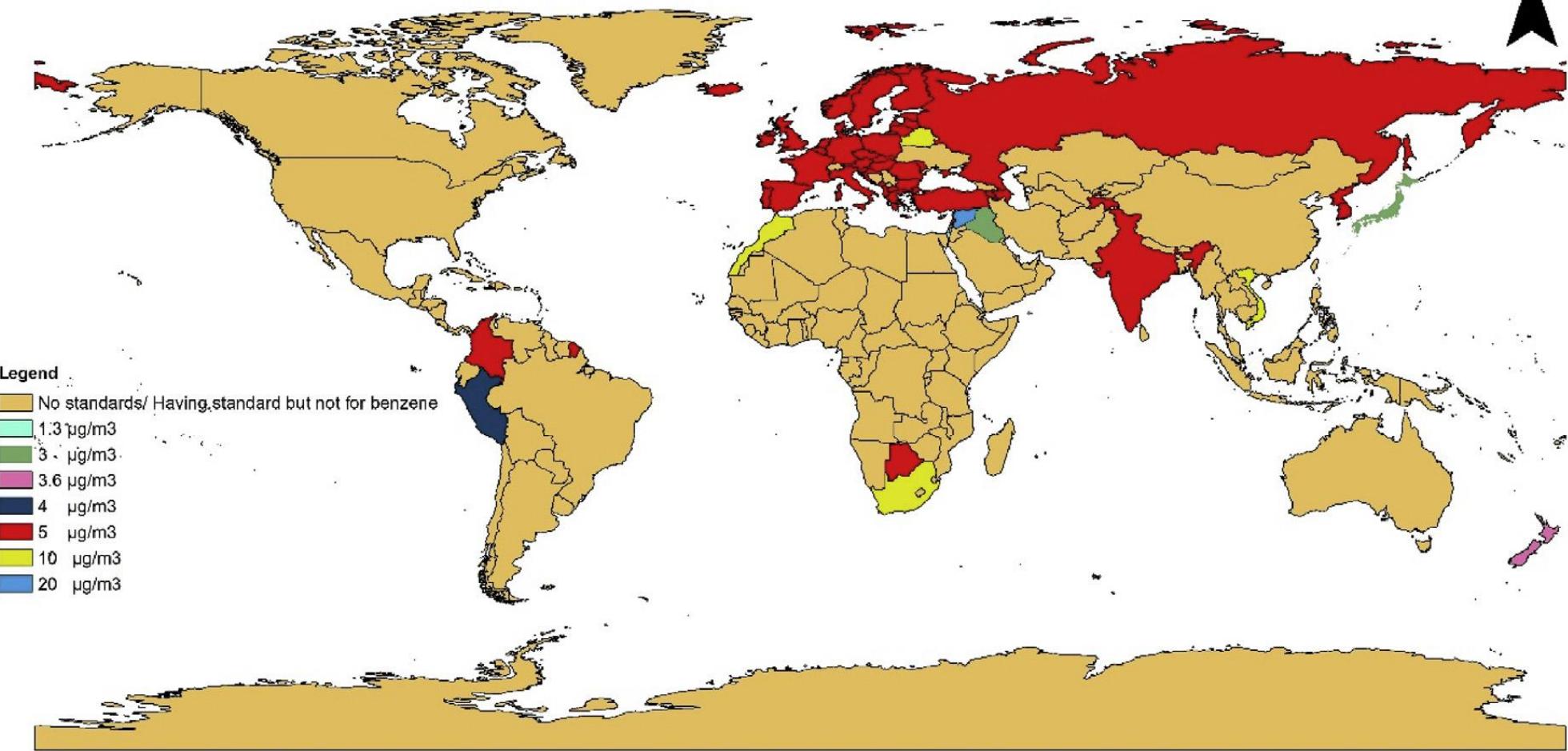
UE: Valores límite para COV

Respecto de la UE, antes existía un límite máximo de COV's de 400 µg/m³, sin embargo, ese límite se eliminó debido a la falta de documentación de problemas a la salud, y entonces se estableció un valor límite para Benceno de 5 µg/m³ (Directiva UE 2008/50/CE), es decir se norma como contaminante criterio.

El Benceno es el único BTEX que ha sido catalogado como Cancerígeno.

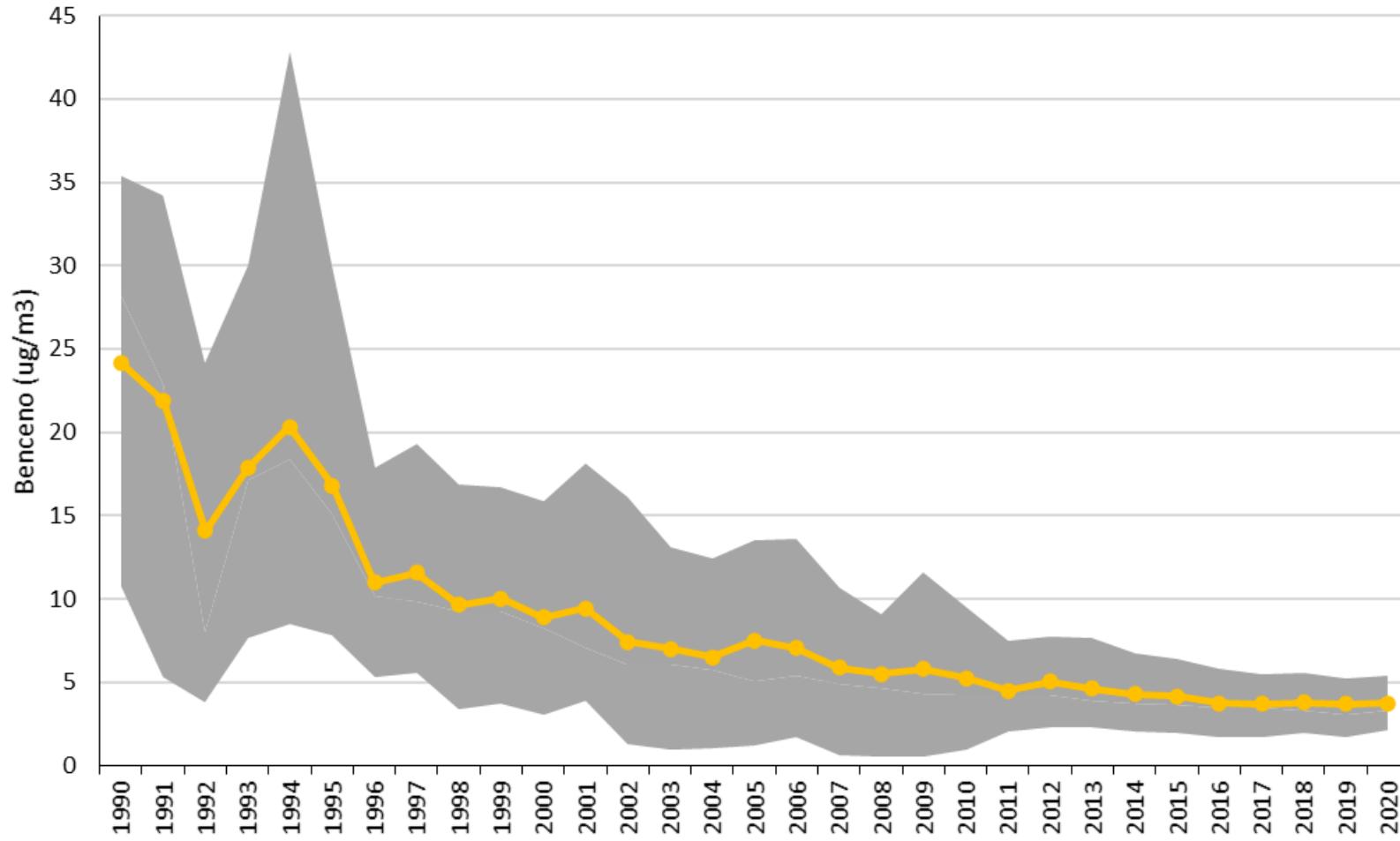
NILU, 2019

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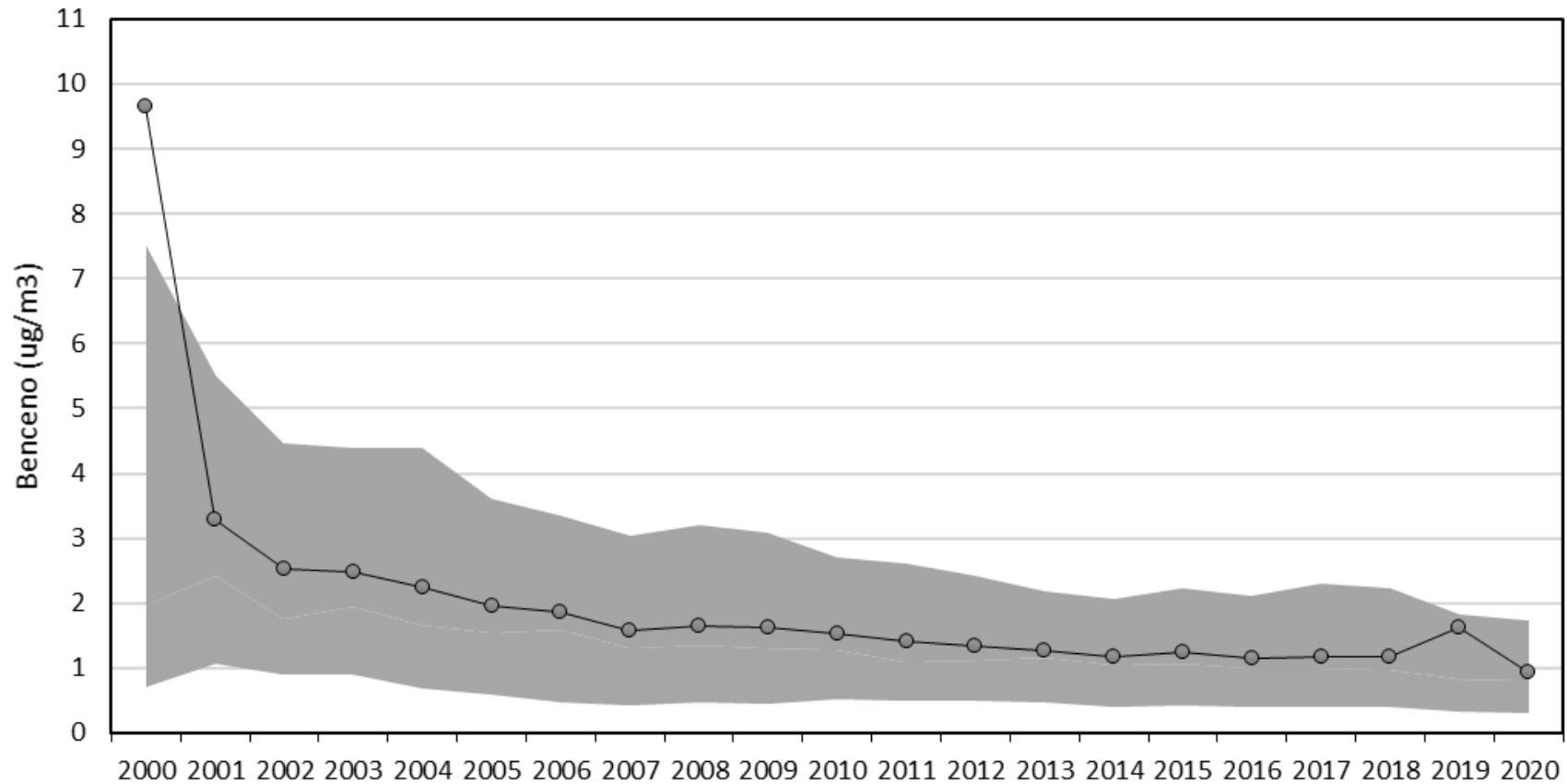


USA

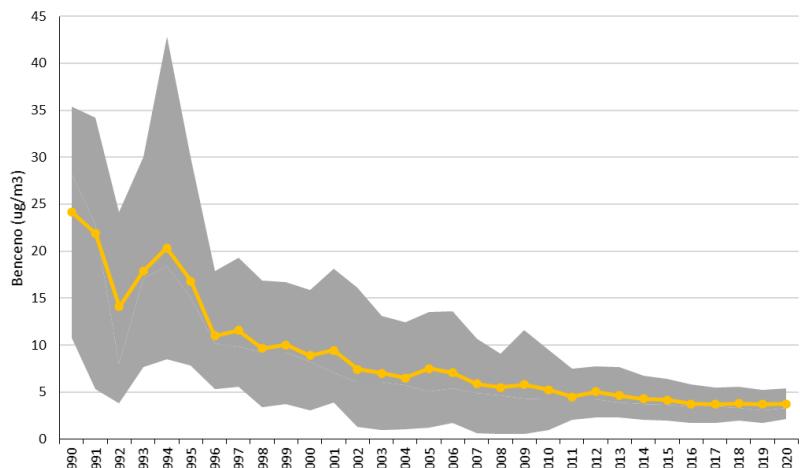
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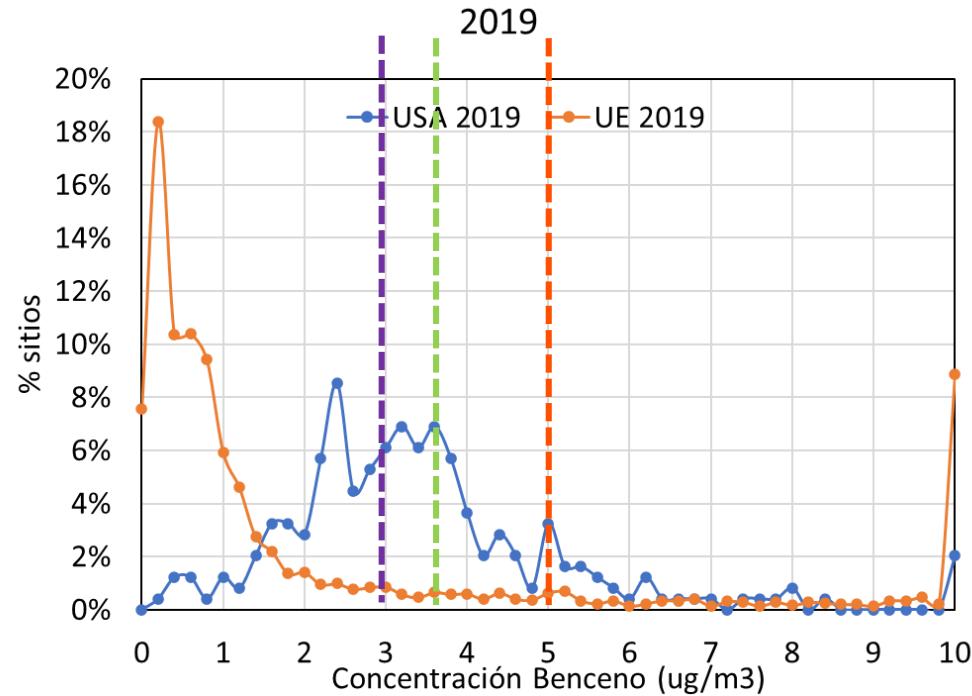
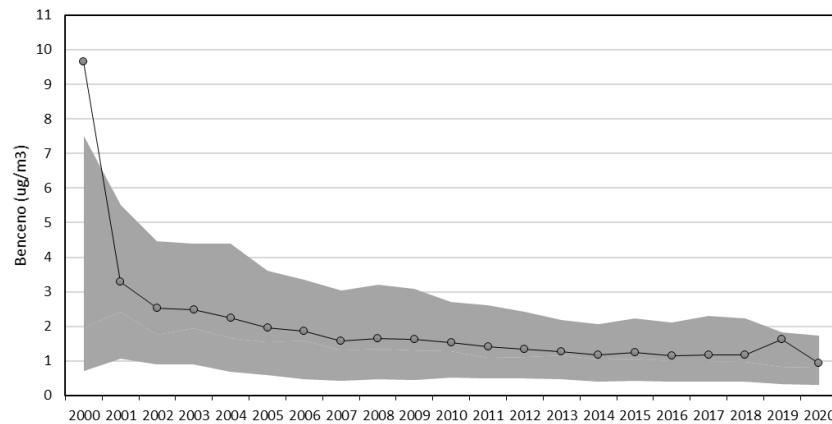
UE



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UE



2015 U.S. EPA Petroleum Refinery rule: Medición de emisiones fugitivas de Benceno

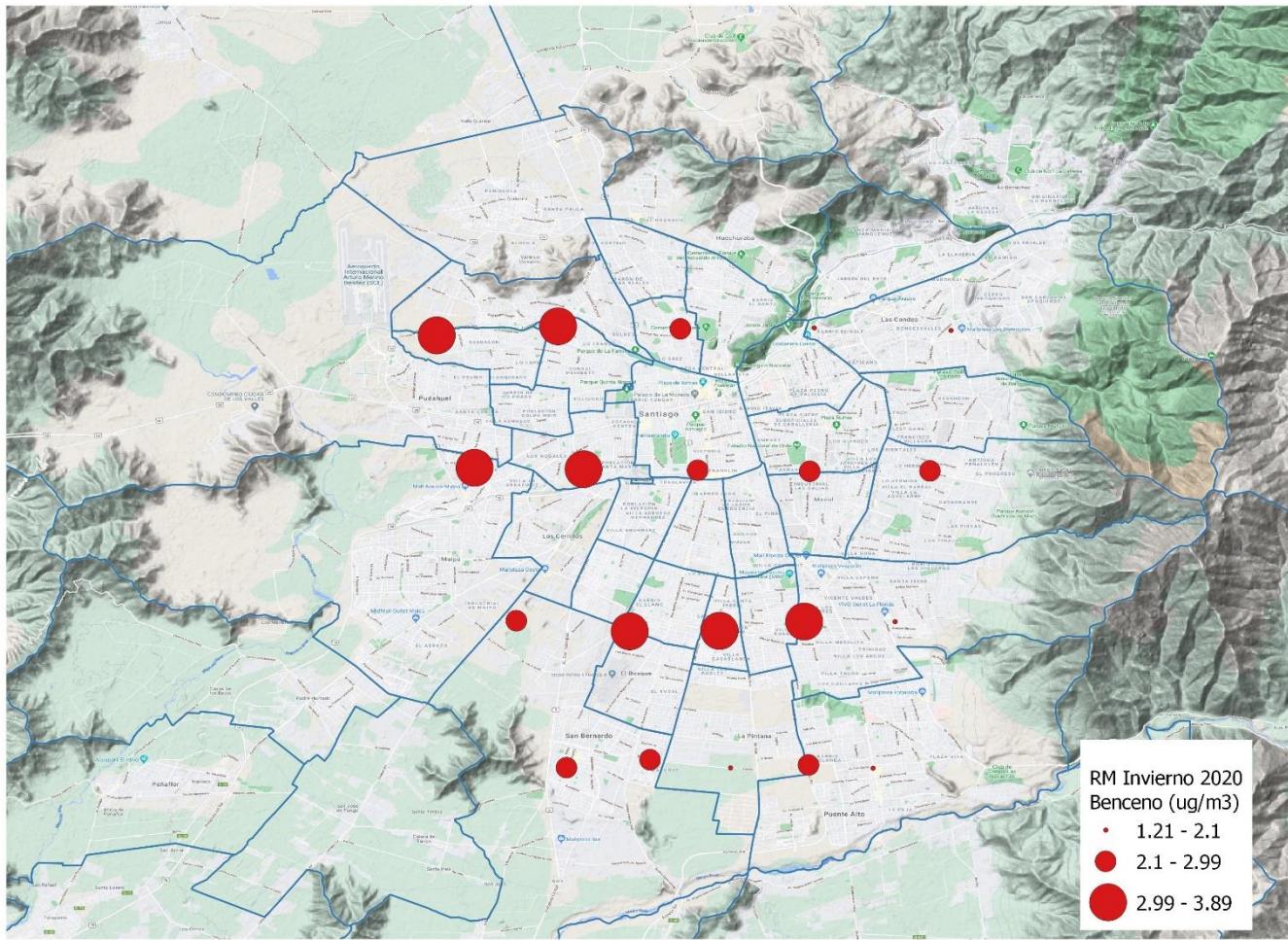
Desde 2018 las refinerías deben medir la concentración promedio de benceno alrededor del perímetro de las plantas (“fenceline”) para verificar el cumplimiento de límite de $9 \mu\text{g}/\text{m}^3$ (anual).



Fuente: OPSIS AB

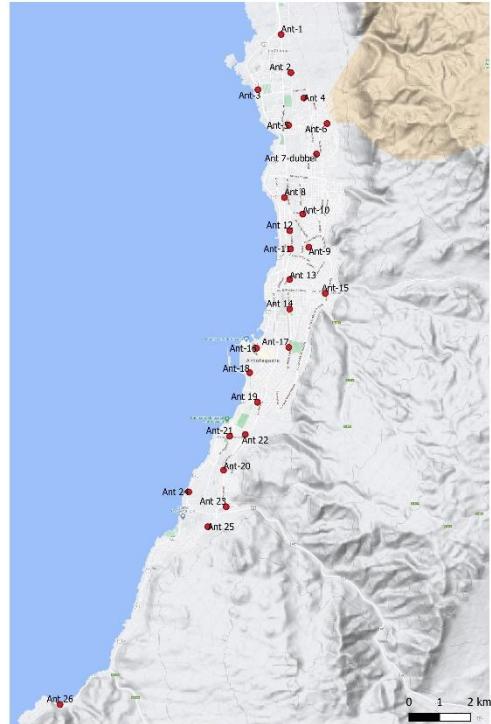
INFORMACIÓN NACIONAL

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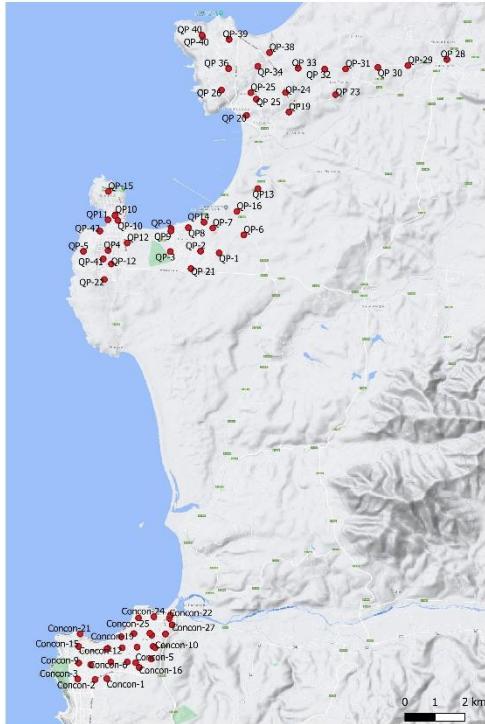


RM

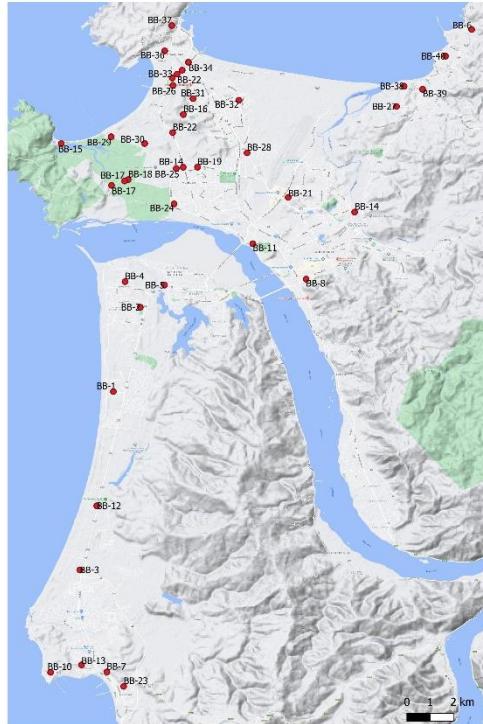
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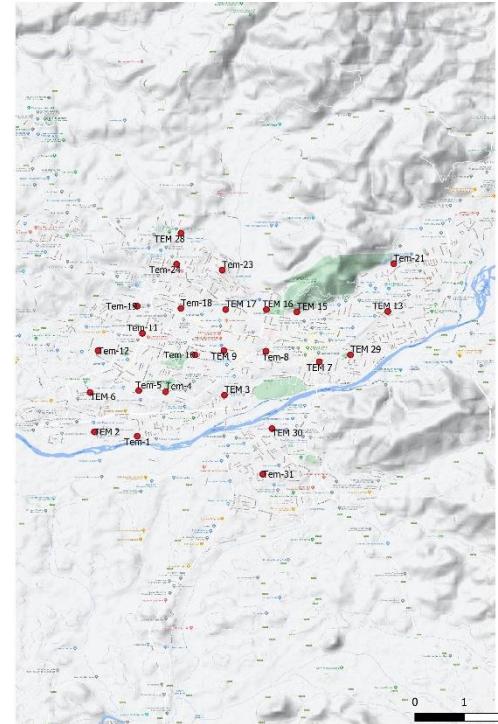
Antofagasta



PQC



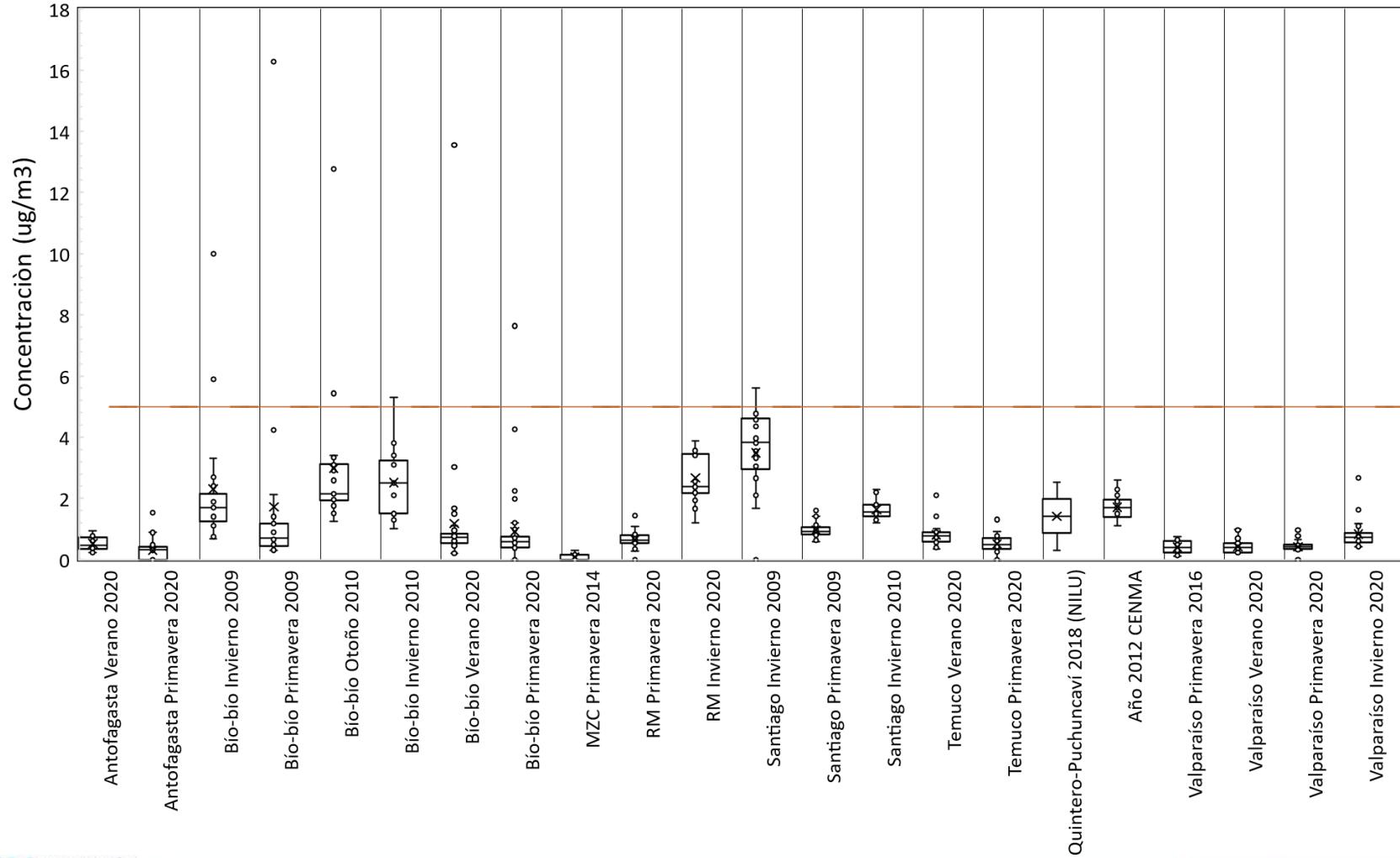
Concepción,
Talcahuano,
Hualpén



Temuco,
Padre Las
Casas

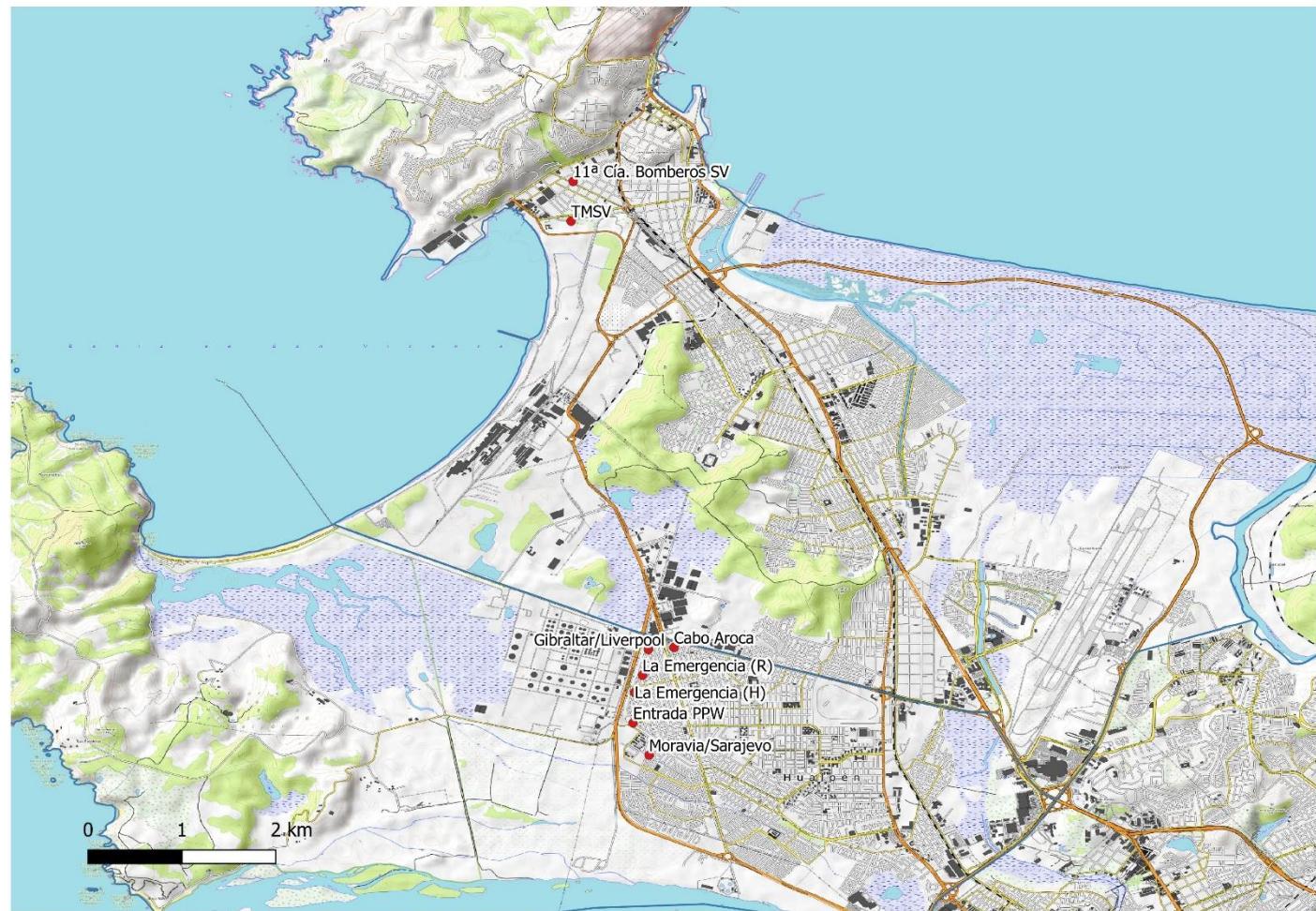
Benceno

001181 vta



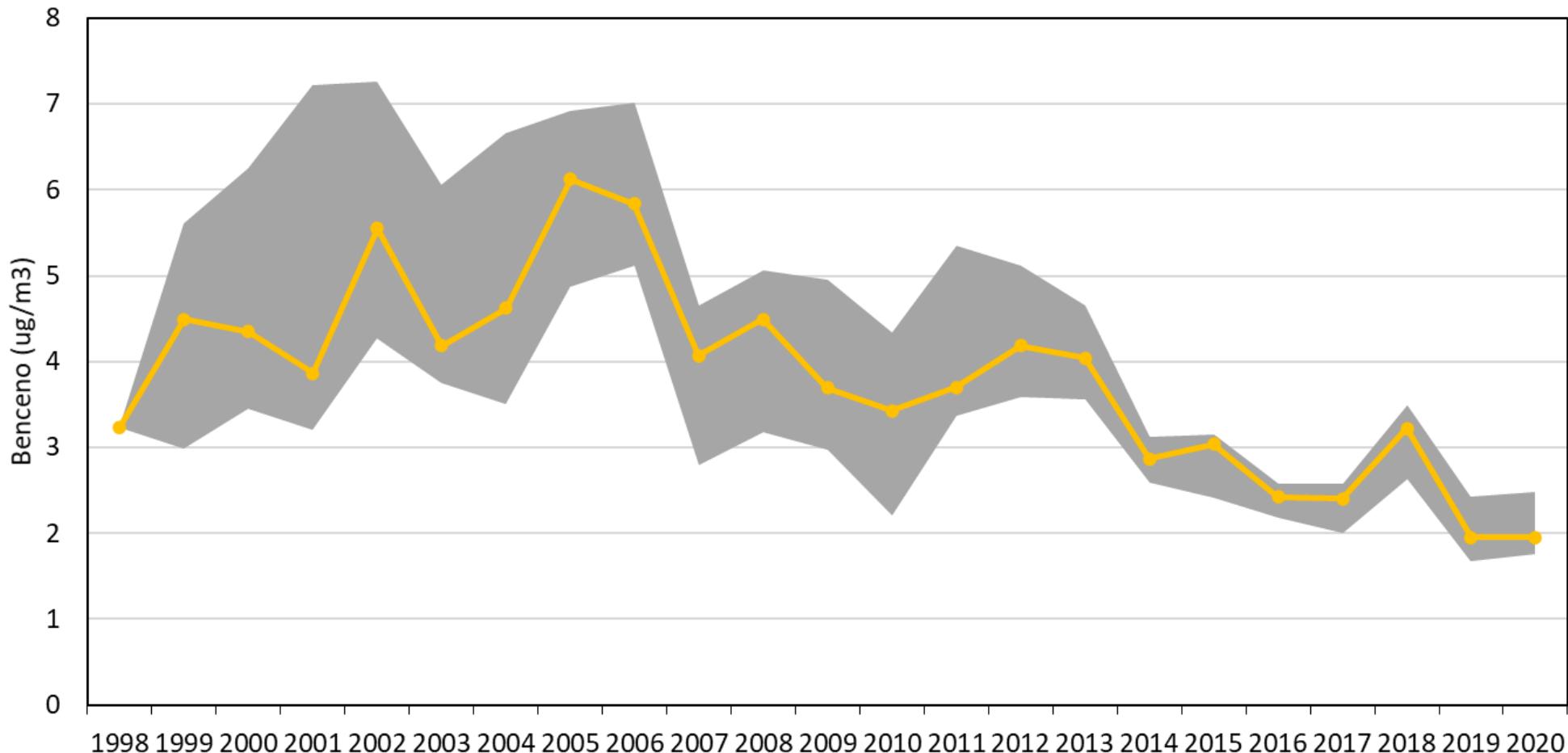
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Talcahuano-Hualpén 1998-2020



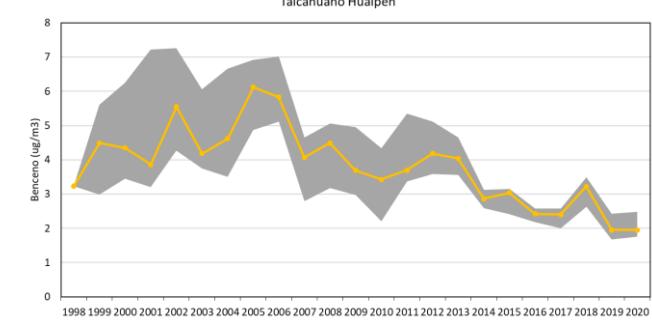
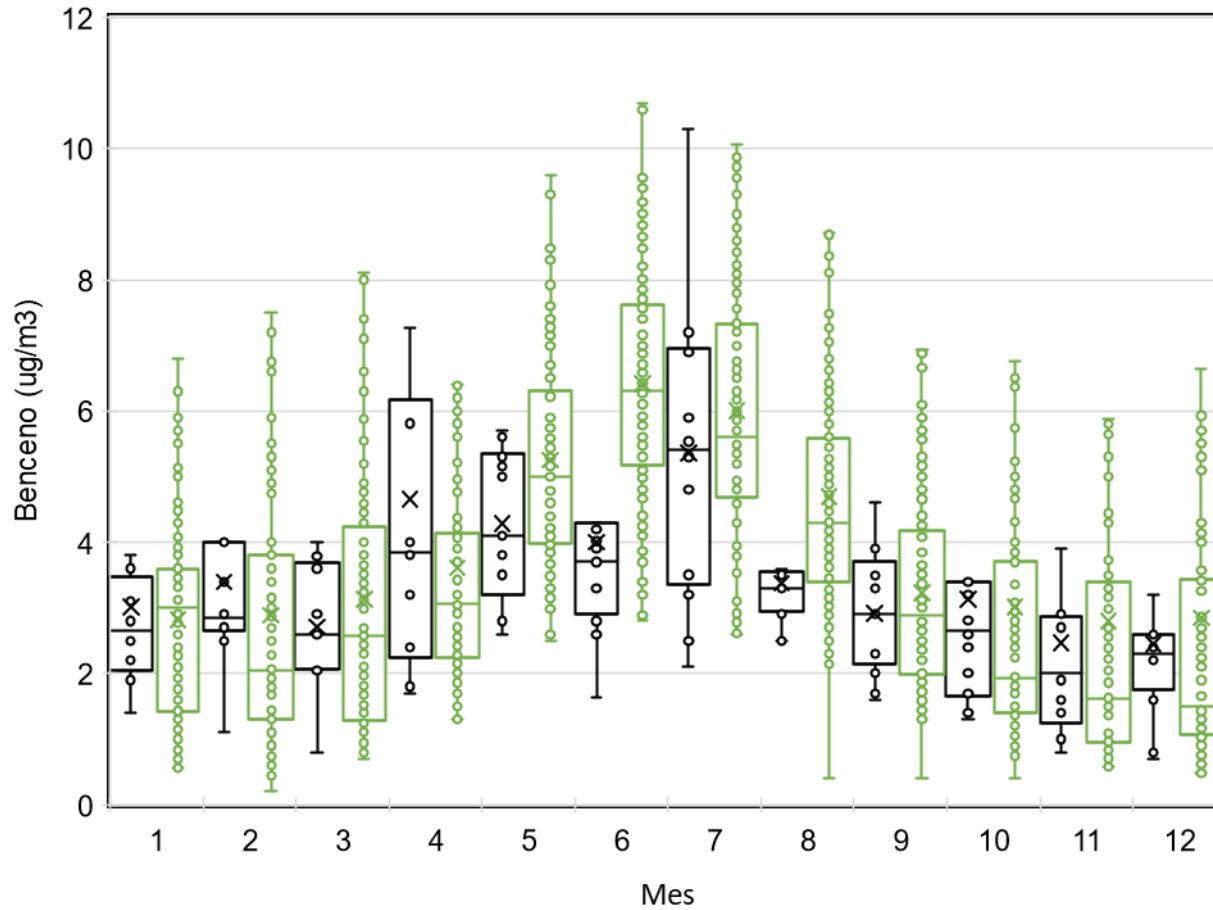
Talcahuano Hualpen

001182 vta



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□ Talcahuano □ Hualpén



Estacionalidad anual dada por fuentes emisoras y condiciones meteorológicas

Hot-spot en Talcahuano

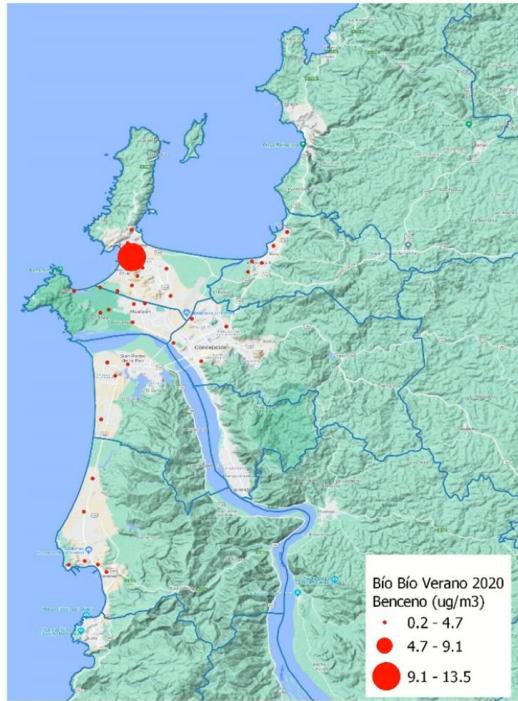


Figura 5: Concentración de Benceno para campañas realizadas en la Región del Bío-Bío durante el año 2020.

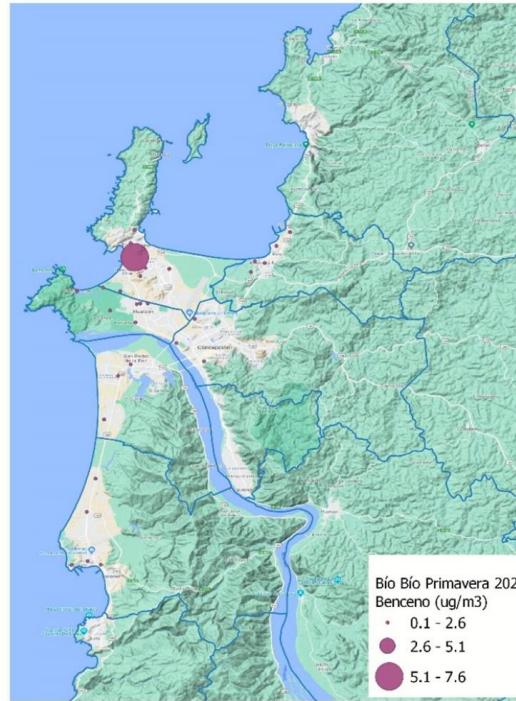


Figura 4: Concentración de Benceno para campañas realizadas en la Región del Bío-Bío durante el año 2010.



Resumen

- BTEX son los COVs más abundantes atmosféricos y son de origen antropogénico.
- La tendencia internacional la mayoría de los países es normar solo al Benceno como estándar de calidad.
- A pesar de tener diferente enfoque regulatorio, hay una tendencia a la disminución tanto en la UE como en EEUU.
- El Benceno es el único BTEX científicamente asociado a cáncer (leucemia).

SISTEMAS DE MONITOREO DE COVs PARA PROPÓSITOS REGULATORIOS

USEPA: Compendio de métodos para la determinación de compuestos tóxicos orgánicos en el aire.

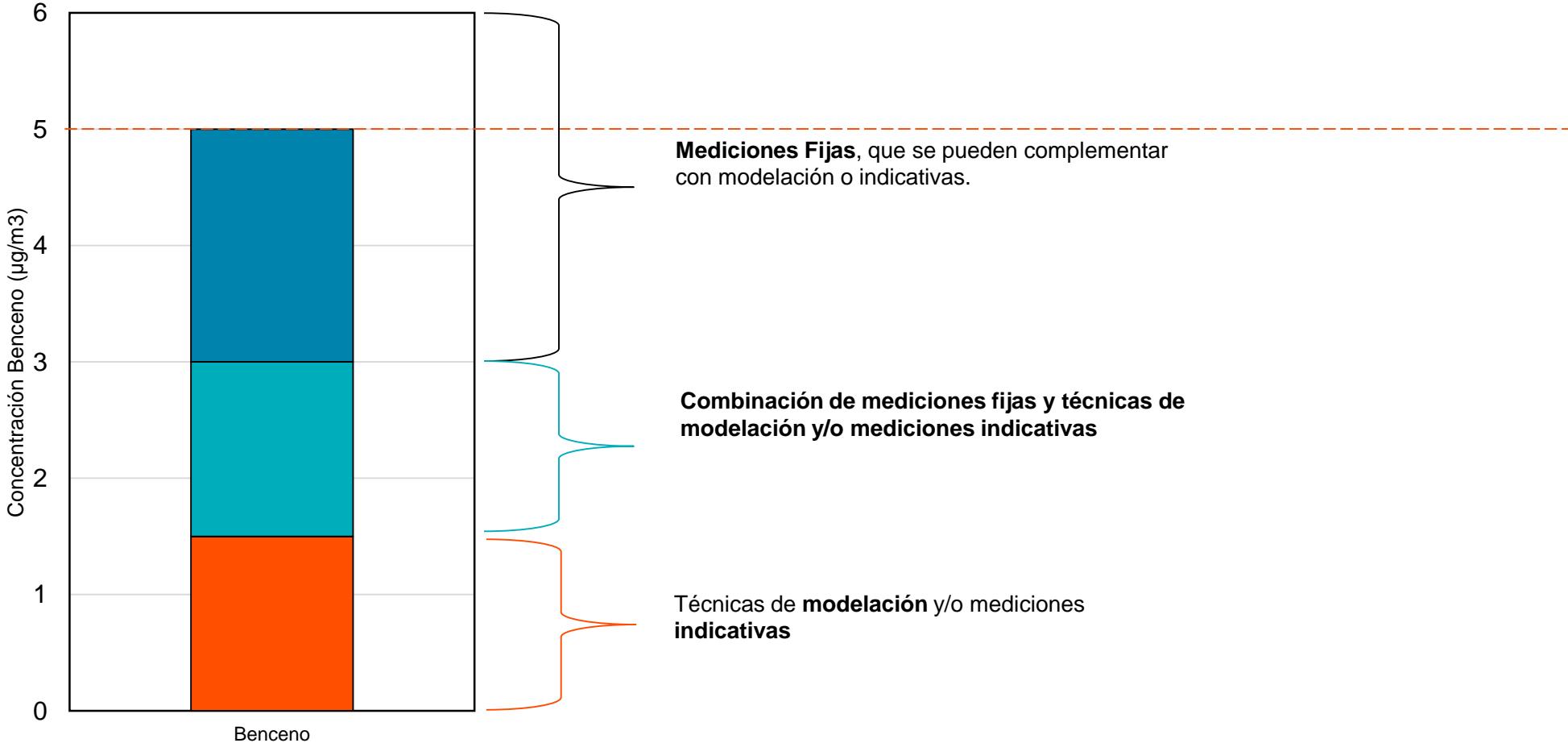
Detalle	Dispositivo de colección	Metodología analítica
TO-1	Sorbente sólido Tenax®	GC/MS
TO-2	Sorbebente molecular	GC/MS
TO-3	trampa Cryo	GC/FID
TO-14A	Canister especialmente tratado	GC/MS o GC/MD
TO-15A	Canister	GC/MS
TO-16	Open Path	FTIR
TO-17	Múltiples adsorbentes	GC/MS, FID, etc

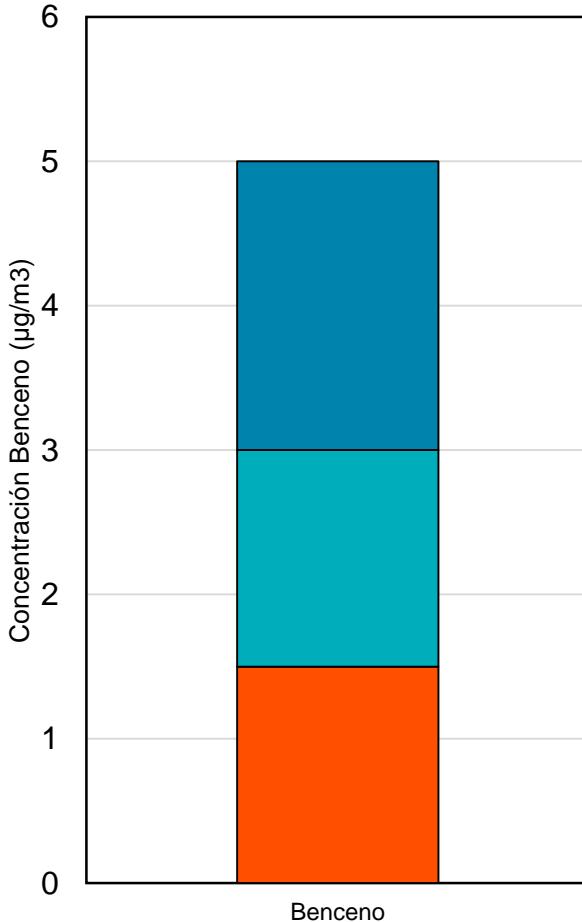
UNIÓN EUROPEA

Detalle	Detalle
UNE-EN 14662-1:2006	Parte 1: Muestreo por aspiración seguido de desorción térmica y cromatografía de gases.
UNE-EN 14662-2:2006	Parte 2: Muestreo por aspiración seguido de desorción por disolvente y cromatografía de gases.
UNE-EN 14662-3:2016	Parte 3: Muestreo automático por aspiración con cromatografía de gases in situ.
UNE-EN 14662-4:2016	Parte 4: Muestreo difusivo seguido de desorción térmica y cromatografía de gases.
UNE-EN 14662-5:2006	Parte 5: Muestreo difusivo seguido de desorción por disolventes y cromatografía de gases.

Alternativas de tecnologías disponibles







Nivel de evaluación	Mediciones Fijas	Mediciones indicativas	Modelación	Estimación objetiva
Incertidumbre	25%	30%	50% (media anual)	100%
Captura mínima de datos	90%	90%	-	-
Cobertura temporal	35% (Fondo urbano y de tráfico) 90% (Emplazamientos industriales)	14%	-	-

IVL utiliza 20 mediciones semanales al año, de manera tal de estar seguros de cumplir con los requerimientos mínimos de la norma en caso de pérdida de datos.

Opinion: Insights into updating Ambient Air Quality Directive (2008/50EC)

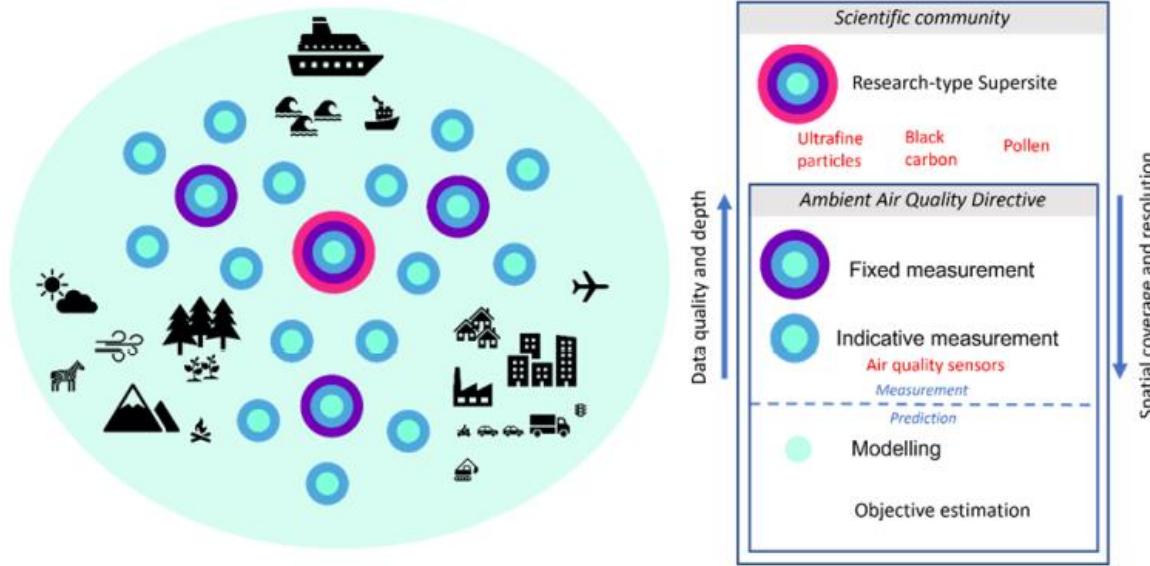
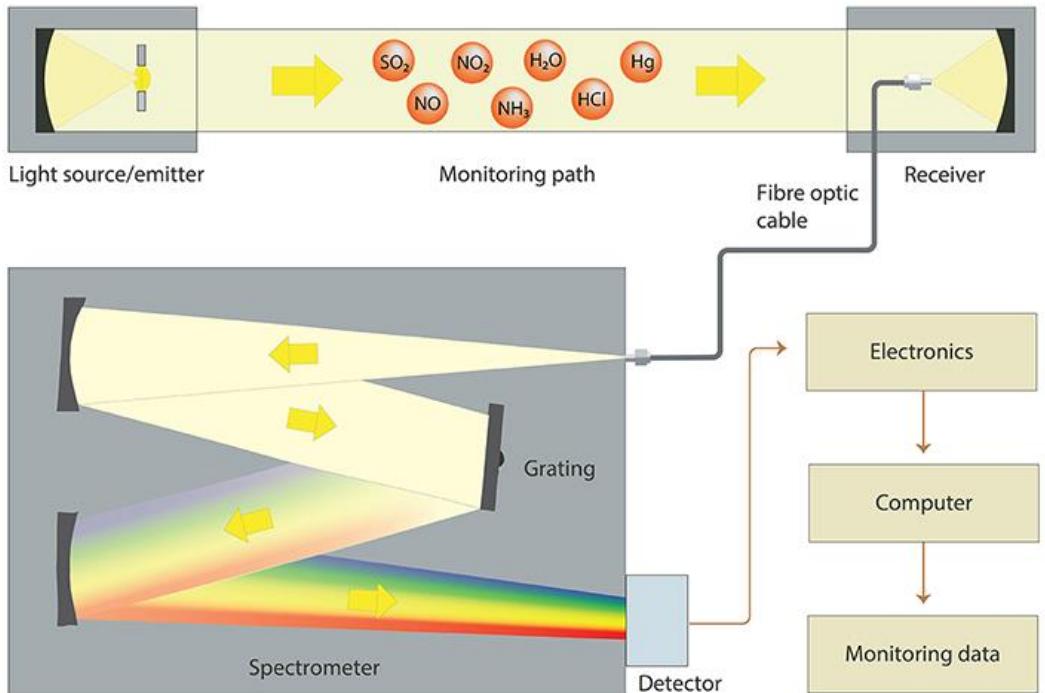


Figure 1: Concept map of air quality monitoring, which combines both regulatory measurements as well as the research-type Supersite stations.

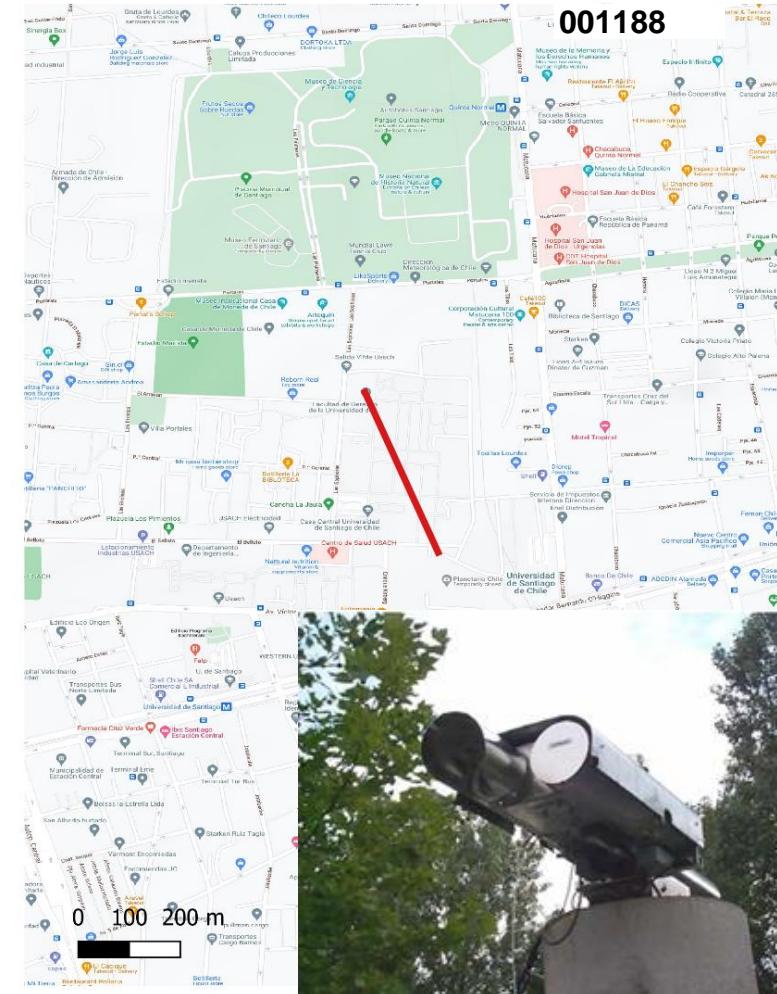
Kuula, J., Timonen, H., Niemi, J. V., Manninen, H., Rönkkö, T., Hussein, T., Fung, P. L., Tarkoma, S., Laakso, M., Saukko, E., Ovaska, A., Kulmala, M., Karppinen, A., Johansson, L., and Petäjä, T.: Opinion: Insights into updating Ambient Air Quality Directive (2008/50EC), Atmos. Chem. Phys. Discuss. [preprint], <https://doi.org/10.5194/acp-2021-854>, in review, 2021.

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UV DOAS



OPSIS®



UV DOAS

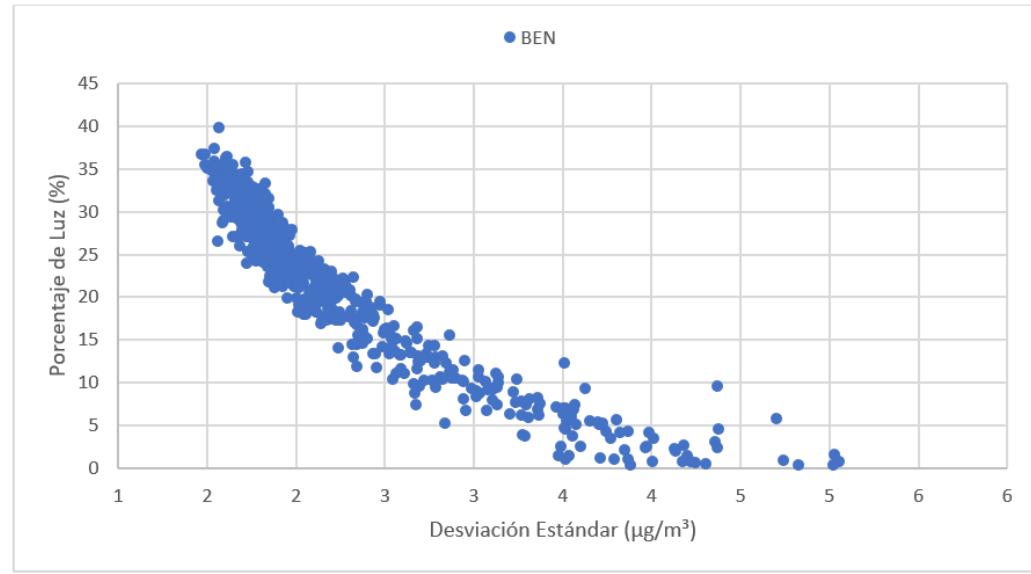
El equipo se configuró para medir: benceno, tolueno, p-xileno, etilbenceno y otros gases.

Parámetros entregados por el equipo:

- Concentración.
- Desviación estándar.
- Porcentaje de luz.

Validación de los datos:

- La relación gráfica de desviación estándar y el porcentaje de luz permite asegurar la calidad del dato, determinando porcentaje de luz sobre el que los datos son confiables.
- En ocasiones el equipo entregó concentraciones negativas, debido que se está midiendo bajo su límite de detección.



Por ejemplo, para el benceno es un 12 %.



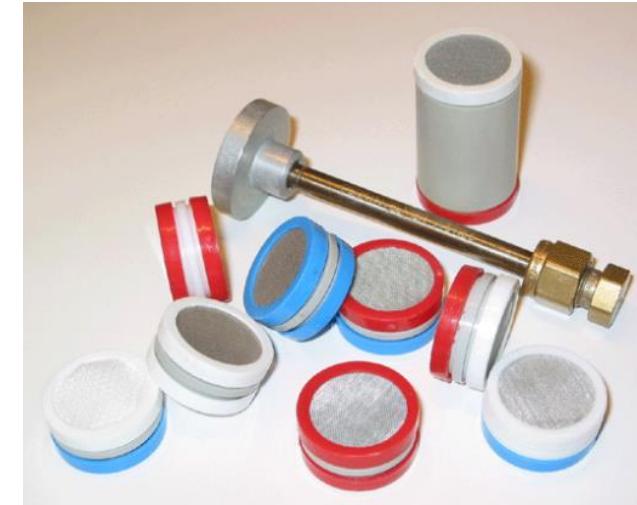
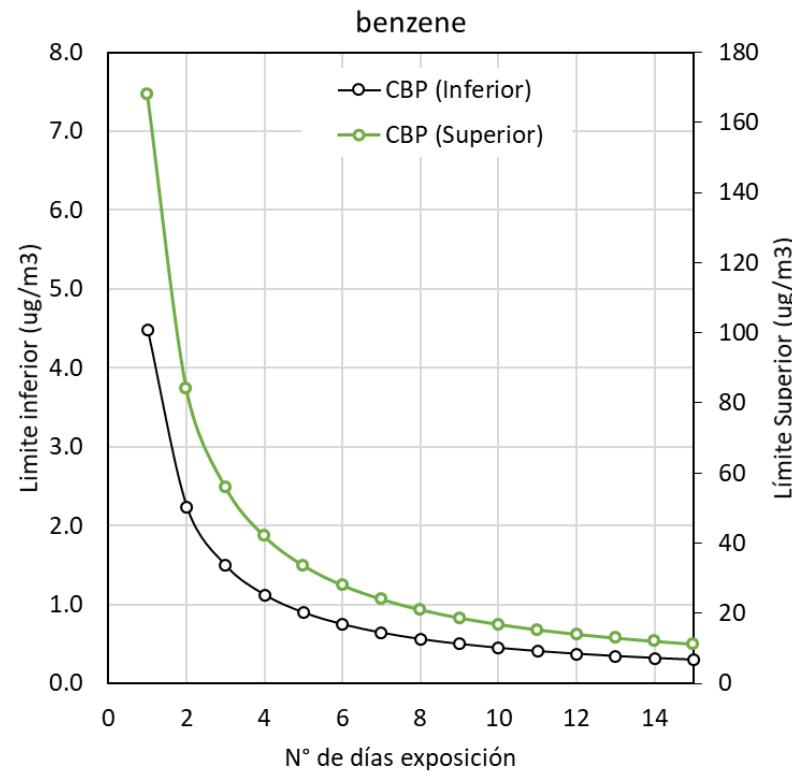
Tubos Pasivos



Dispositivo capaz de tomar muestras de gases o vapores desde la atmósfera a una velocidad controlada por procesos físicos tales como difusión a por medio de una capa estática de aire o un material poroso o permeable a través de una membrana, pero que no requiere de un movimiento activo de aire a través del dispositivo.



Tubos Pasivos



Martin Ferm

Sensores



Los LCS de fotoionización “PID-AH2” se basa en la exposición de la muestra gaseosa a una luz ultravioleta de alta energía, la cual ioniza positivamente las moléculas rompiendo sus enlaces.



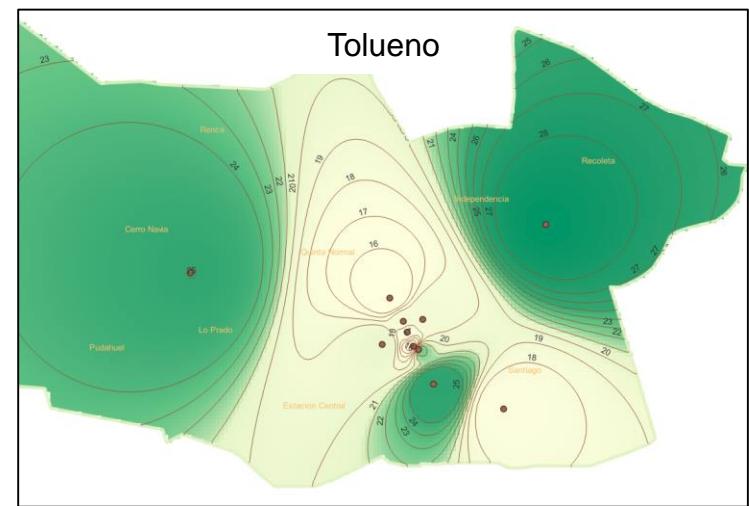
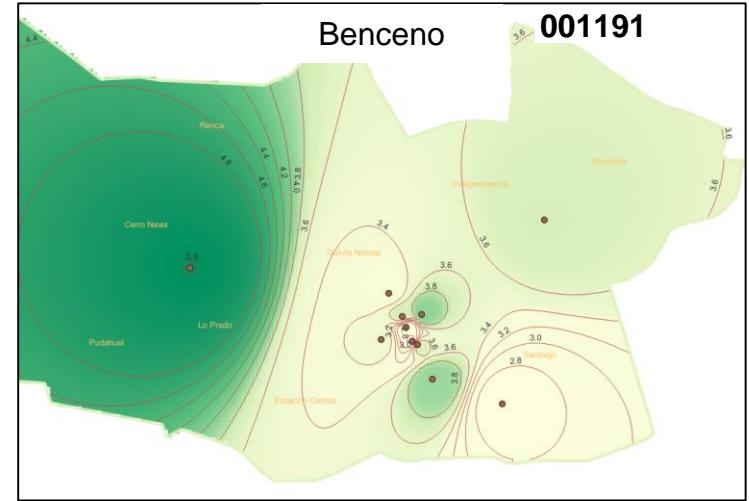
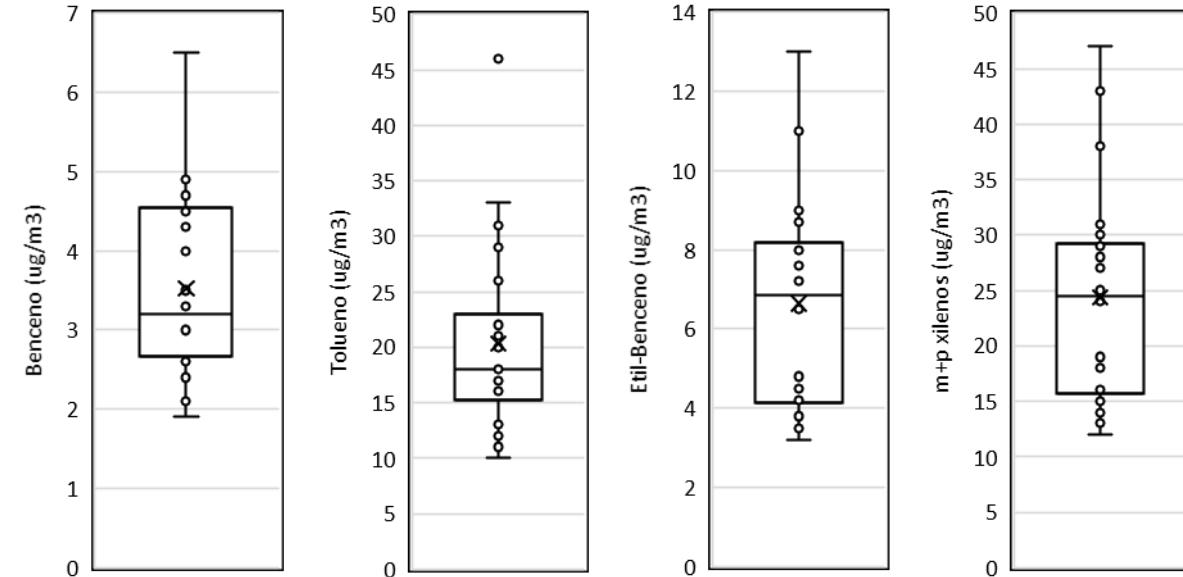
- La conversión de la señal de sensor a unidades de concentración se realizó aplicando un modelo de regresión lineal simple. (Hagan et al., 2018).
- El modelo relaciona la concentración real del gas dada por el instrumento de referencia DOAS a una señal en unidades de voltaje.

Comparación entre tecnologías

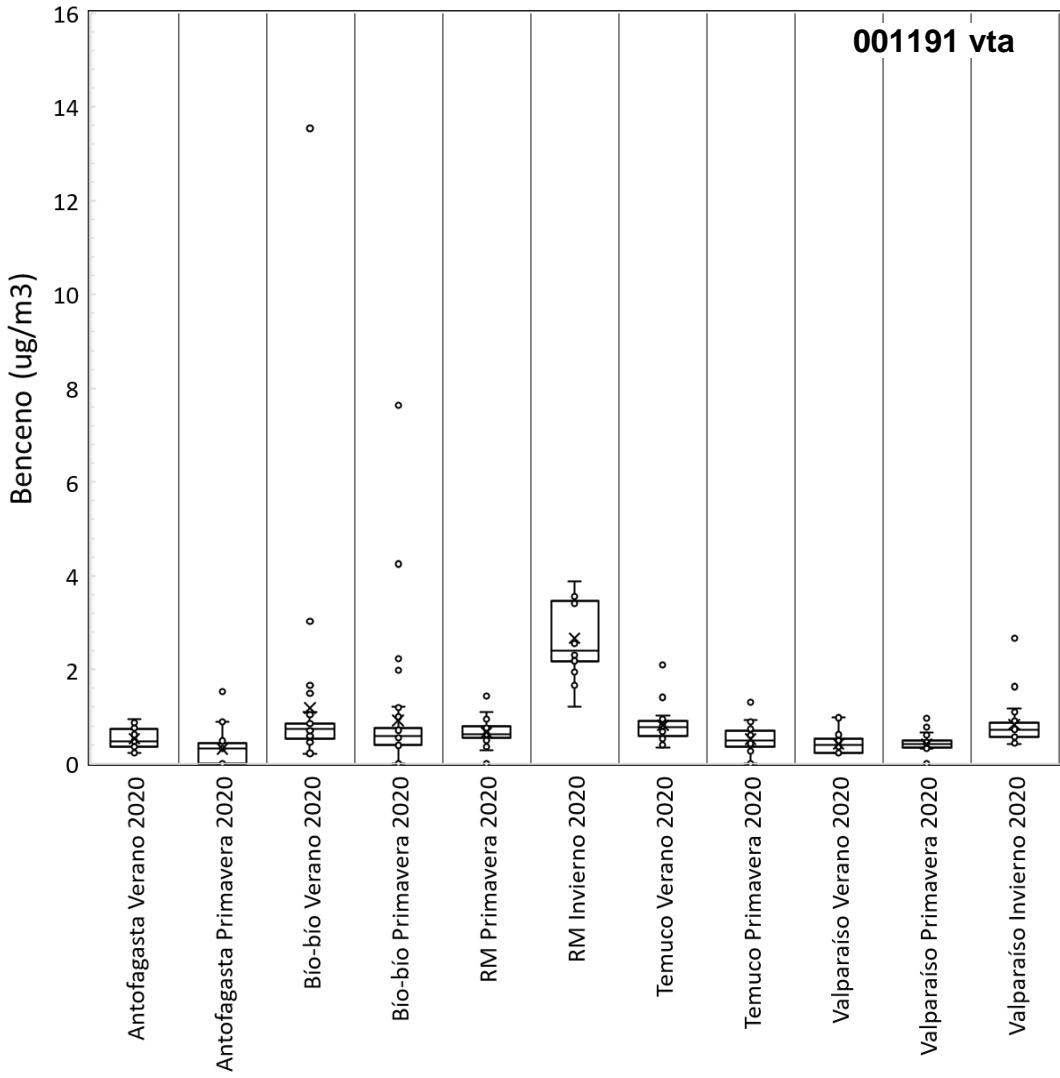
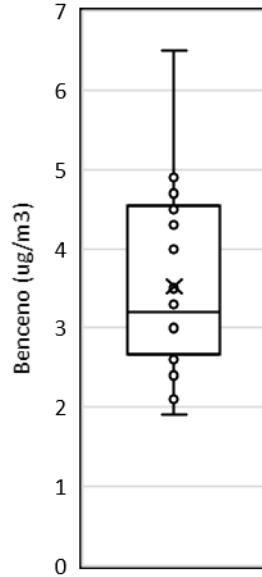
Comparación de concentraciones ($\text{ug}\cdot\text{m}^{-3}$) para los gases benceno, tolueno, etilbenceno y xileno

	DOAS	Tubo pasivo 1 Api USACH	Tubo pasivo 2 Matemáticas	Sensores		
				COV20	COV23	COV24
Benceno	2,2	2,75	2,55	3,12	3,40	3,34
Tolueno	21,0	17,5	14,0	12,12	11,4	11,44
Etilbenceno	6,3	5,75	5,75	4,14	3,79	3,77
Xileno	7,8	7,6	21,0	7,37	9,04	9,09

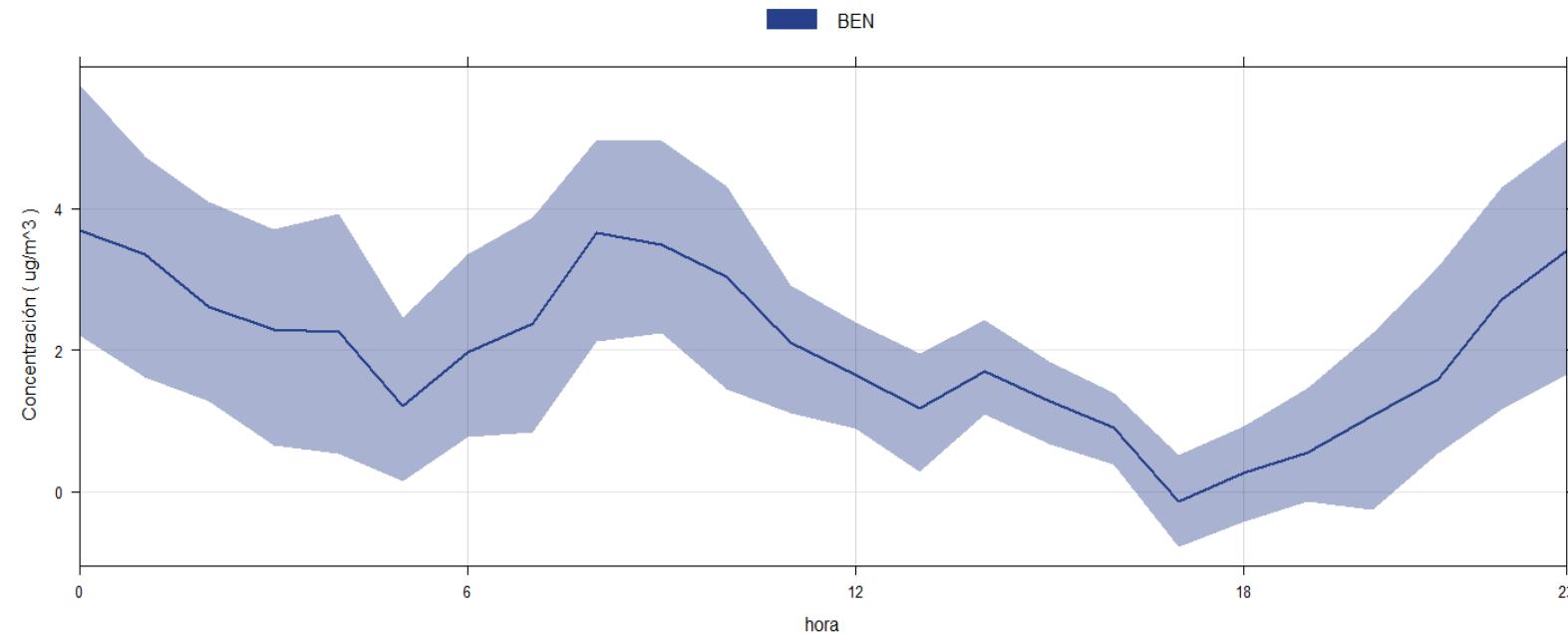
DISTRIBUCIÓN ESPACIAL



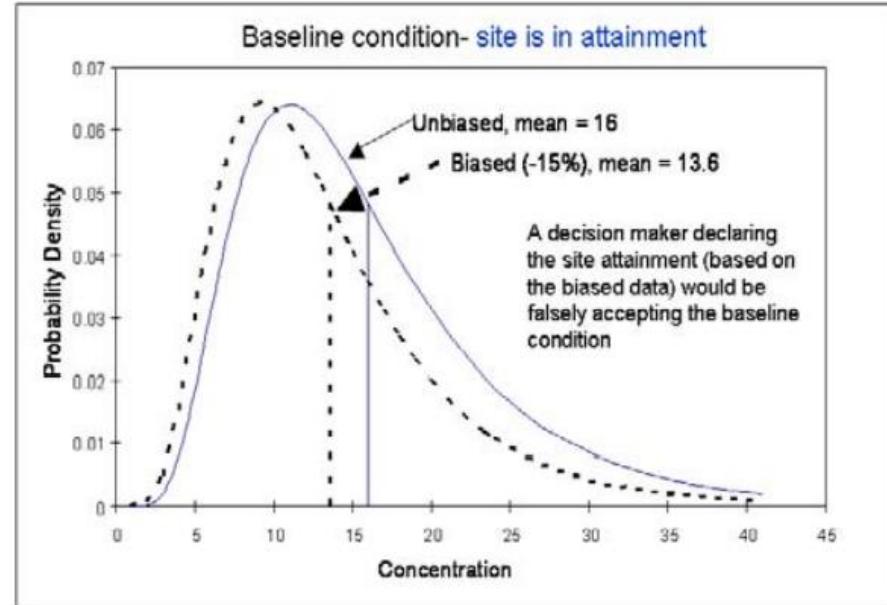
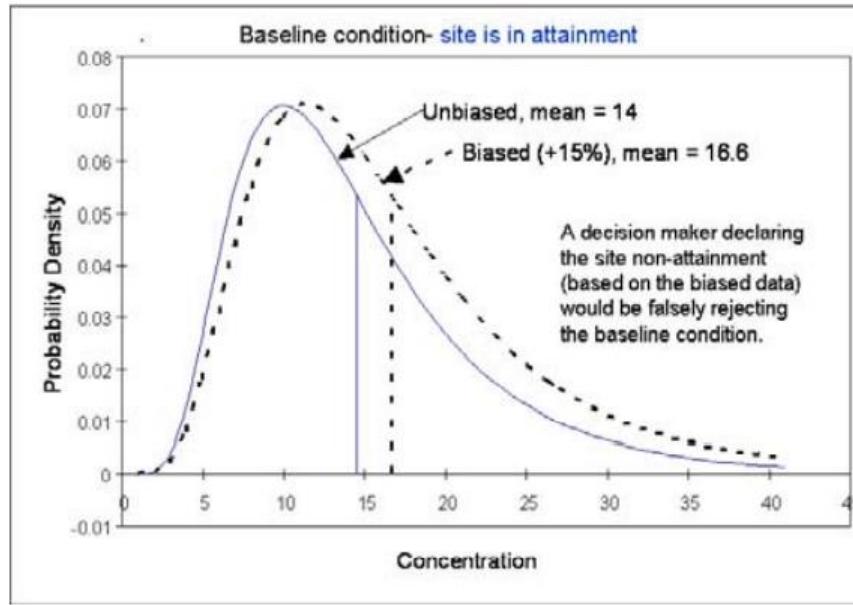
COMPARACIÓN



Perfil Diurno Benceno



Las mediciones nunca están libres de errores



$$S_{Total}^2 = S_{población (espacial y temporal)}^2 + S_{medición (data)}^2$$

RESUMEN

- La medición de COVs es más costosa en comparación con el monitoreo de calidad del aire convencional (Partículas, NO₂, O₃, etc), no solamente por el tipo de instrumental, sino también por la capacidad humana a desarrollar.
- Diferentes alternativas de monitoreo, acorde con diferentes necesidades.
- Las tecnologías aquí utilizadas en la campaña de monitoreo (DOAS, tubos pasivos, sensores) mostraron su **capacidad de entregar datos confiables de medición**, bajo diferentes escenarios.
- El escenario de nivel de Concentración de Benceno más probable en Chile es una situación **bajo el límite de la normativa de la UE (5 µg/m³)**, salvo algunas excepciones.



LABOR LAETITIA NOSTRA



**Centro
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Investigación & desarrollo

A I R F L U X

REVISIÓN DE NORMATIVA INTERNACIONAL y MÉTODOS DE MONITOREO

2da sesión del Comité operativo ampliado del proceso de
elaboración de la Norma primaria de calidad del aire para COVs

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Martes 16 de Noviembre 2021
Santiago, Chile