Characterization and amendment plans f agricultural areas surrounding the Gardanne bauxite processing plant

Giovanni Pagano
ACELAB
Dipartimento di Scienze Chimiche,
Università di Napoli Federico II, Napoli, Italie

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and Toxicology

Effluent from Bauxite Factory Induces Developmental and Reproductive Damage in Sea Urchins

N. M. Trieff[1], L. A. Romaña[2], A. Esposito[3], R. Oral[4], F. Quiniou[2], M. Iaccarino[5], N. Alcock[1], V. M. S. Ramanujam[1], G. Pagano[5]

Abstract. The effluent from a bauxite plant was tested on sea urchin embryos and sperm for the induction of: a) developmental defects in effluent-exposed embryos; b) loss of fertilization success, and c) transmissible damage to the offspring of pre-treated sperm. The chemical composition of the bauxite sludge was analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). Dose-related effects were observed at effluent dilutions ranging from $1:10^5$ to $1:10^2$ [equal to 1.5 to 1,500 µg (dry weight)/ml]. The effects were exerted on developmental toxicity, spermiotoxicity, and offspring malformations/mortality. Toxicity was exerted by sludge concentrations in the order of $1:10^3$ (or 150 µg/ml). Chemical analysis of sludge pointed to the presence of several inorganics, with prevalence of aluminum, iron and chromium. In spite of the recognized difficulties in referring the effects of complex mixtures (bauxite sludge) to the toxicities of individual components, the results reported here are fairly consistent with those reported on the toxicities of the major sludge components. Based on the present data, uncontrolled disposal of bauxite sludge may be a major hazard(s) to the environment, involving early life stages and recruitment in aquatic biota.

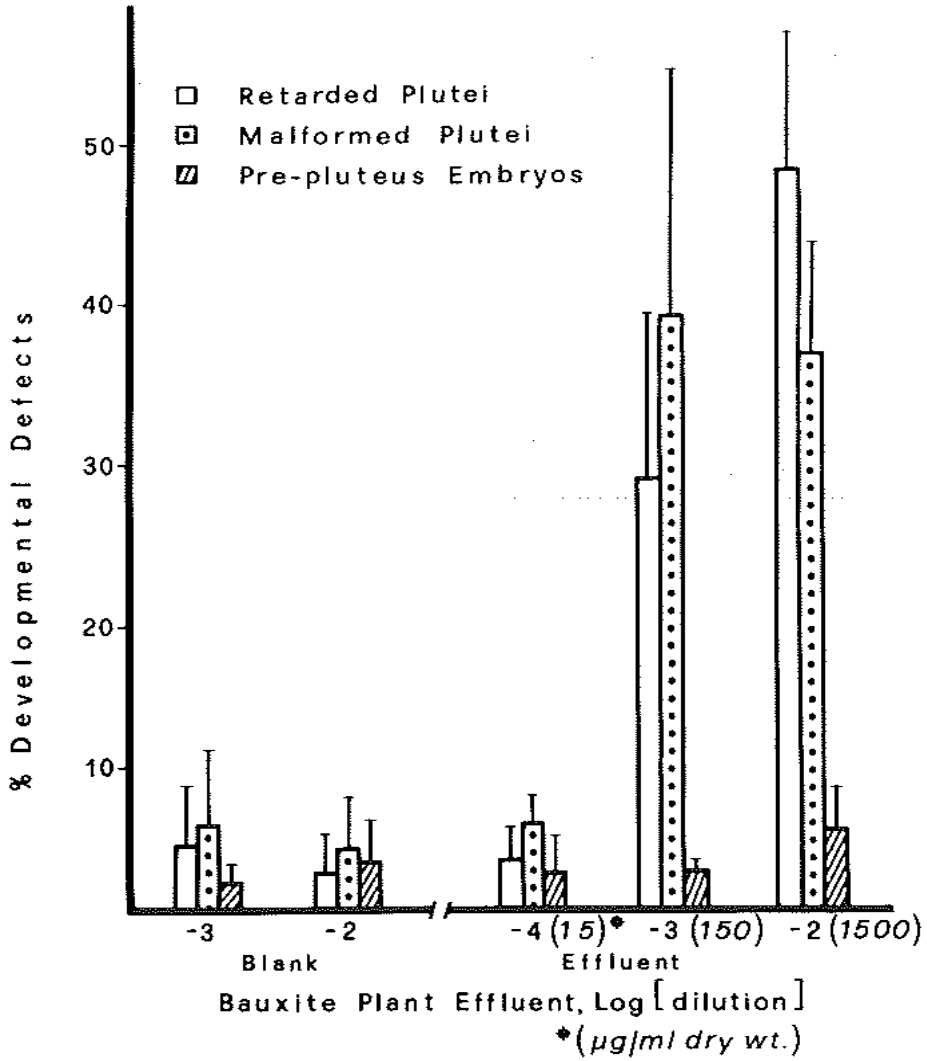

Fig. 1. Dose-response trend of developmental defects in *P. lividus* embryos reared in bauxite sludge. Triplicate experiment

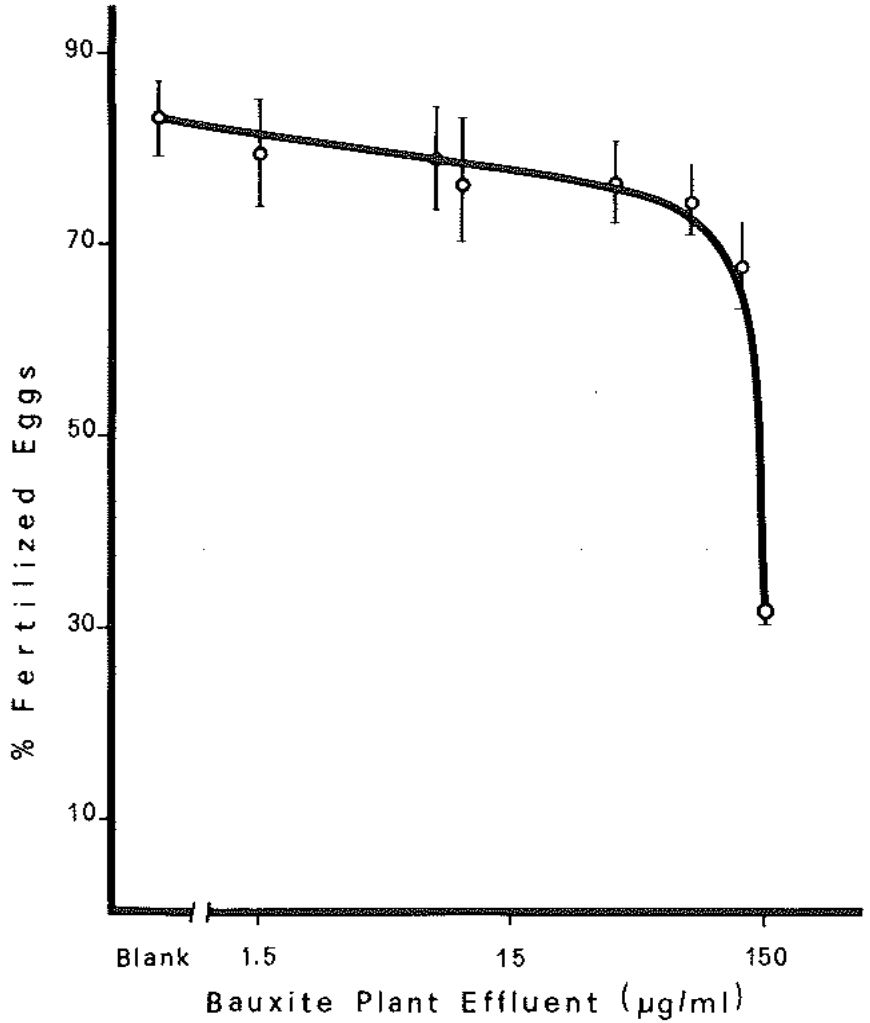

Fig. 2. Bauxite sludge-induced spermiotoxicity following a 30-min exposure of *P. lividus* sperm. Quintuplicate experiment (from ten sperm lots)

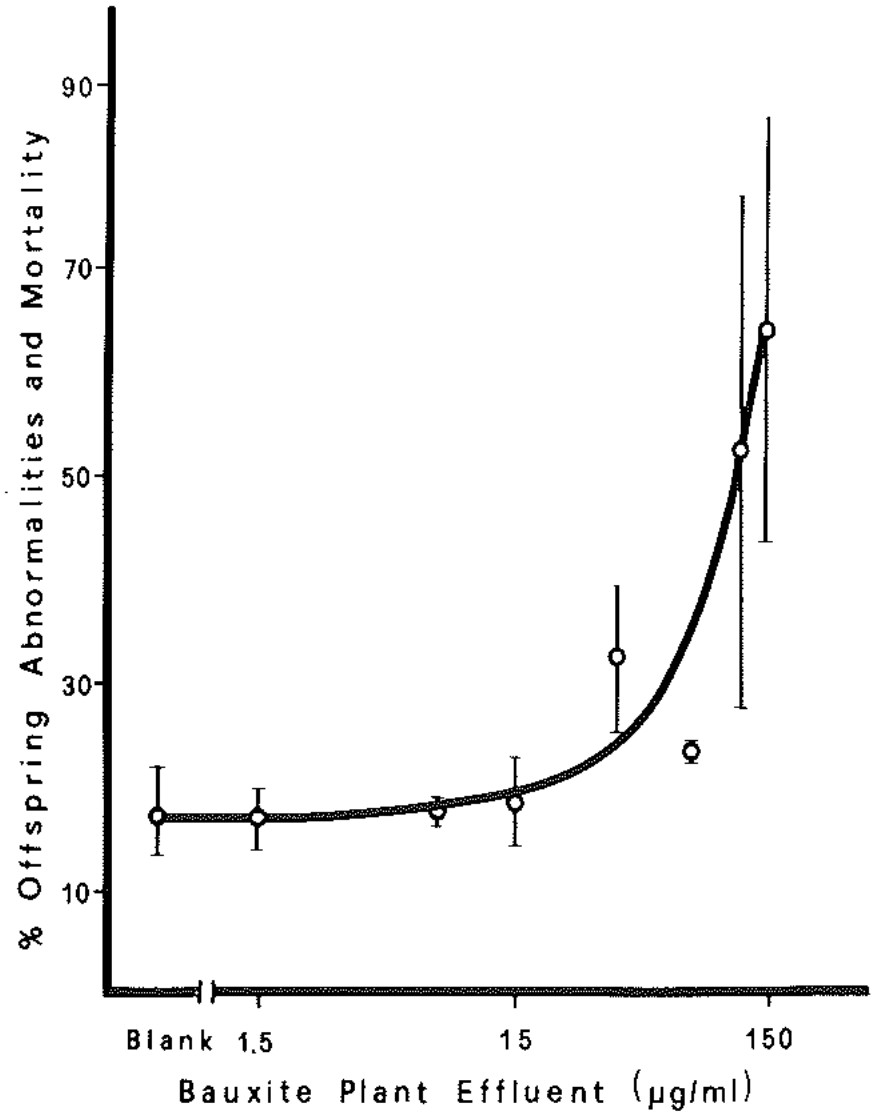

Fig. 3. Together with spermiotoxic effect, the offspring of bauxite sludge-pretreated sperm displayed a dose-response increase in larval abnormalities and mortality

The observation of larval abnormalities and mortality in the offspring of bauxite sludge-exposed sperm may suggest the induction of transmissible damage. Moreover, analogous effects in the offspring of sea urchin and mussel sperm exposed to either aluminum sulfate or iron chloride are consistent with the present data and point to transmissible damage induced by aluminum, iron, and their mixtures (unpublished).

Regardless of the mechanisms involved, bauxite effluent ("red mud") could represent a significant marine or aquatic ecotoxin and should be regulated accordingly.

Ecotoxicology and Environmental Safety 50, 000}000 (2001)

Toxicity of Bauxite Manufacturing By-products in Sea Urchin Embryos

Giovanni Pagano, Süreyya Meriç, Antonella De Biase, Mario laccarino, Domenico Petruzzelli, Olcay Tünay, and Michel Warnau

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BAUXITE MANUFACTURING RESIDUES FROM GARDANNE (FRANCE) AND PORTOVESME (ITALY) EXERT DIFFERENT PATTERNS OF POLLUTION AND TOXICITY TO SEA URCHIN EMBRYOS

GIOVANNI PAGANO,*† ANTONELLA DE BIASE,† MARIO IACCARINO,† SÜREYYA MERIÇ,‡ DOMENICO PETRUZZELLI,§ OLCAY TÜNAY,‡ MICHEL WARNAU,‖ and NORMAN M. TRIEFF#


France
Gardanne
Italy
Portovesme

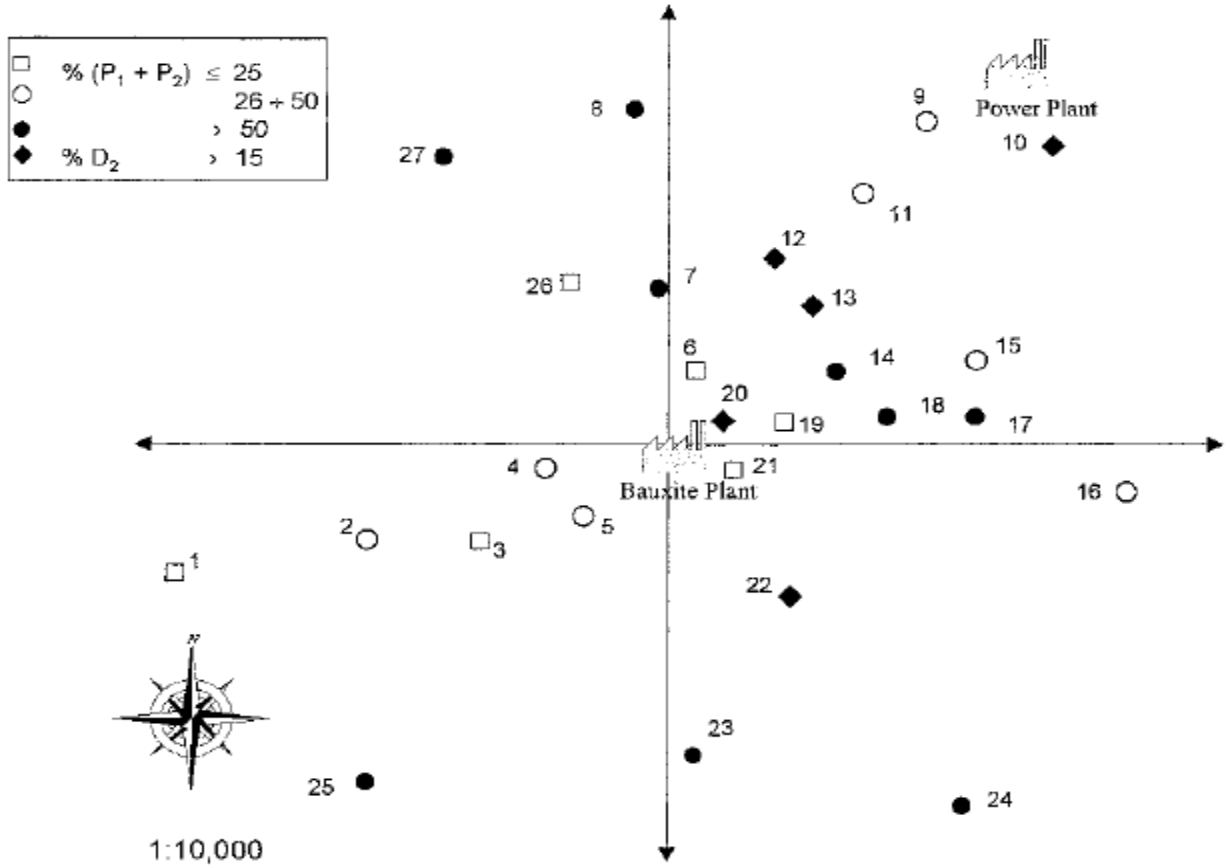

Fig. 2. The topographic distribution of soil and dust samples in Gardanne, France, was centered at the bauxite factory and included the town center and residential and agricultural areas. A coal-fueled power plant was located at the northeast border of Gardanne.

Table 1. Prevalence (%) of larval retardation (R) and developmental arrest (P2) in *Sphaerechinus granularis* embryos reared in bauxite plant particulate (G20) from Gardanne, France

No. treatment schedule	%	R	P2
Blank		7.0 ± 2.0	1.0 ± 1.0
G20	0.1	10.0 ± 4.0	7.0 ± 3.0
	0.5	37.5 ± 8.5	29.0 ± 3.0
	1.0	Cytolysis	

Table 3. Concentrations of some selected inorganics from Gardanne, France, dust (G20) sample following strong-acid extraction (SAE [as mg/kg]) seawater extraction (SWE [as μg/L]) at the levels of 0.2 and 1 g/100 ml for 24 h. A bauxite sample was also analyzed by SWE. Measurements were carried out at the wavelengths specified below. Other elements were at levels below detection limits (μg/L): Cd < 2, Ni < 3, Pb < 30, Sb < 30, and Te < 30

Samples	Extraction procedure	Al (λ = 396.2)	Cu (λ = 324.8)	Fe (λ = 238.2)	Mn (λ = 257.6)	Zn (λ = 213.8)
G20	SAE	117,047	15	31,102	177	103
	SWE 0.2	45	6	14	6	3
	1.0	114	7	101	31	4
Bauxite	SWE 0.2	241	6	166	3	2
	1.0	244	7	190	3	3

Table 2. Prevalence (%) of fertilization success (FR) and offspring quality (R and P2) following *Sphaerechinus granularis* 10-min sperm exposure to G20 particulate

No. treatment schedule	%	FR	R	P2
Blank		52.0 ± 5.0	11.8 ± 7.4	5.4 ± 1.9
G20	0.1	44.0 ± 7.0	13.6 ± 4.7	19.0 ± 15.3
	0.5	33.0 ± 7.0	23.0 ± 5.9	25.0 ± 3.1
	1.0	33.0 ± 5.0	11.8 ± 5.2	36.0 ± 11.4

Table 5. Prevalence (%) of developmental defects in *Sphaerechinus granularis* larvae reared in soil samples (0.5% w/v) collected below the cablecar track close to the Portovesme, Italy, bauxite plant at different distances from the seaside (industrial dock). The sample 150PP was collected at 150 m from seaside, close to the power plant (PP). Quadruplicate experiment. R = % retarded larvae; P1 = % malformed larvae; P2 = % embryos unable to undergo larval differentiation

Distance from seaside (m)	R	P1	P2
Blank	6.2 ± 2.9	3.7 ± 0.8	2.3 ± 0.4
Cd(II) 2.5×10^{-4} M	0.0 ± 0.0	0.0 ± 0.0	100.0 ± 0.0
5	0.0 ± 0.0	0.0 ± 0.0	100.0 ± 0.0
15	0.0 ± 0.0	0.0 ± 0.0	100.0 ± 0.0
50	10.3 ± 1.3	21.8 ± 1.3	9.8 ± 2.8
100	5.3 ± 3.1	10.0 ± 2.2	1.3 ± 0.6
150	1.5 ± 0.6	59.3 ± 19.5	39.3 ± 19.9
150PP	0.0 ± 0.0	0.0 ± 0.0	100.0 ± 0.0

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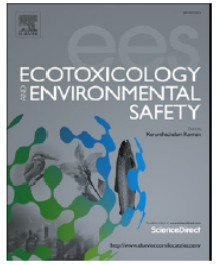


Soil pollution and toxicity in an area affected by emissions from a bauxite processing plant and a power plant in Gardanne (southern France)

Rahime Oral[a], Giovanni Pagano[b,c,*], Antonietta Siciliano[b], Maria Toscanesi[b], Maria Gravina[b], Aldo Di Nunzio[b], Anna Palumbo[c], Philippe J. Thomas[d], Franca Tommasi[e], Petra Burić[f], Daniel M. Lyons[g], Marco Guida[b], Marco Trifuoggi[b]

A B S T R A C T

Soil pollution and toxicity have been investigated in the Gardanne area (southern France) at a range of sites around a recognized pollution source, a bauxite processing plant (BPP), and a power plant (PP). Soil samples were submitted to inorganic and organic analyses and tested for toxicity in two invertebrate models. Inorganic analysis was based on determining elemental concentrations by ICP-MS, encompassing a total of 26 elements including 13 rare earth elements (REEs), of the soil samples and their leachates after 24 or 48 h in seawater. Organic analyses were performed by measuring the sums of 16 polycyclic aromatic hydrocarbons (PAHs) and of total hydrocarbons (C-10 to C-40). Bioassays were carried out on the early life stages of three sea urchin species (*Arbacia lixula*, *Paracentrotus lividus* and *Sphaerechinus granularis*), and on a nematode (*Caenorhabditis elegans*). Sea urchin bioassays were evaluated by the effects of soil samples (0.1–0.5% dry wt/vol) on developing embryos and on sperm, and scored as: a) % developmental defects, b) inhibition of sperm fertilization success and offspring damage, and c) frequencies of mitotic aberrations. *C. elegans* 24 h-mortality assay showed significant toxicity associated with soil samples. The effects of soil samples showed heightened toxicity at two groups of sites, close to the BPP main entrance and around the PP, which was consistent with the highest concentrations found for metals and PAHs, respectively. Total hydrocarbon concentrations displayed high concentrations both close to BPP main entrance and to the PP. Further studies of the health effects of such materials in Gardanne are warranted.

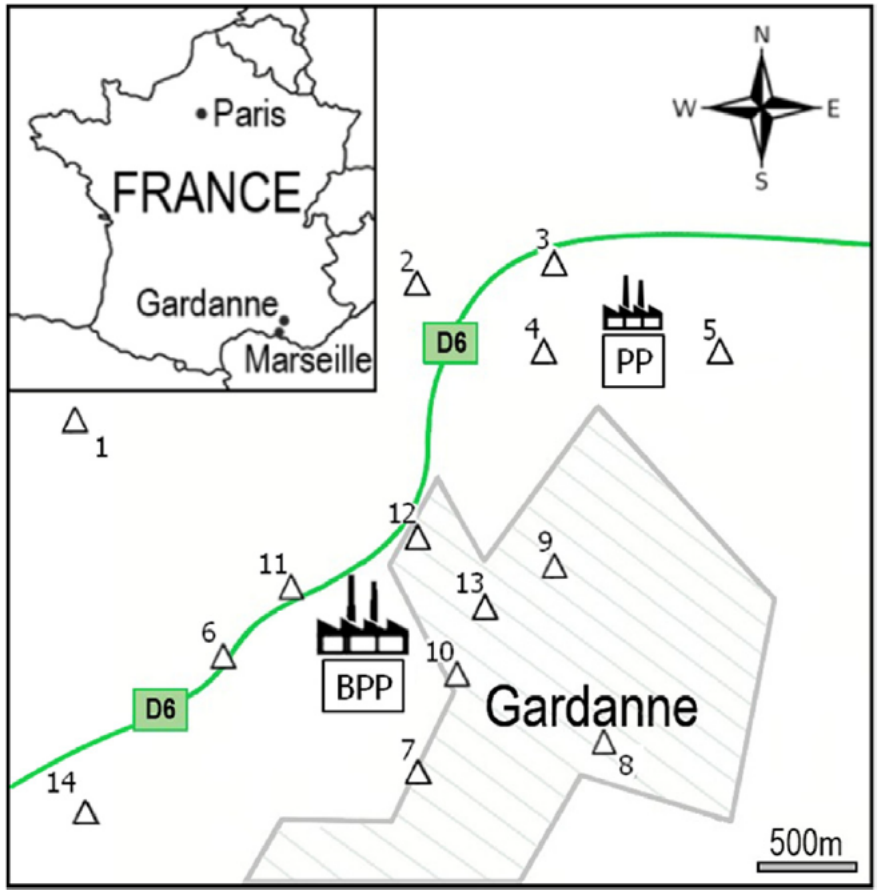
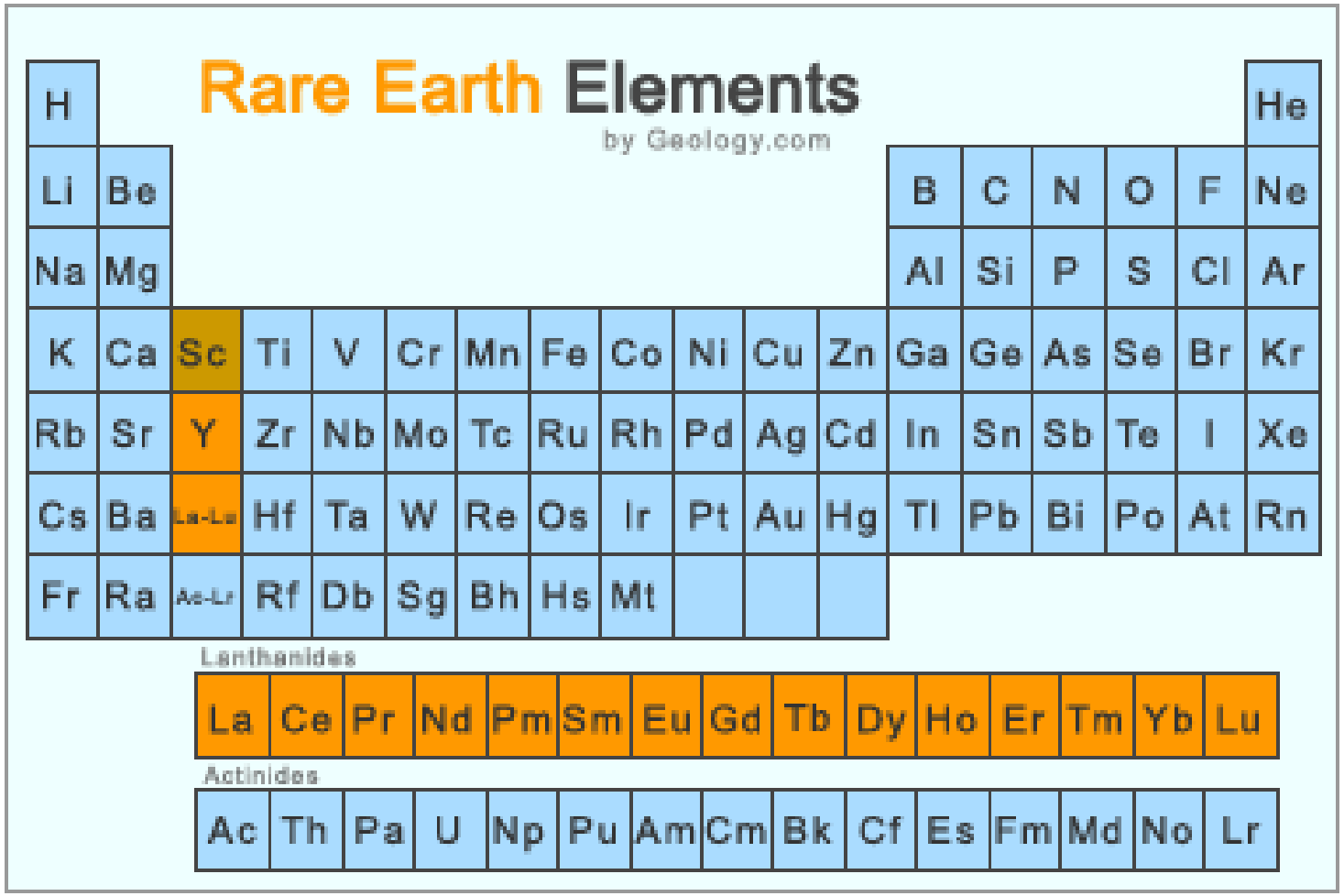


Fig. 1. Map of Gardanne (40°26'46" N 79°58'56" W), southern France, and of soil sampling points. Abbreviations: BPP – Bauxite Processing Plant; PP – Power Plant.

3.1. Inorganic analysis

Following acid oxidative digestion, metal concentrations were measured in soil samples. Iron and aluminum displayed the highest concentrations (> 1000 mg/kg) in samples from sites 1, 8, 9 and 13. Lower concentrations were found for Mn with a range of 18–34 mg/kg noted among the sites. The sum of REE concentrations showed the third highest concentration at all the sites, with the highest concentrations of 20–25 mg/kg noted at sites 1, 8 and 9. The other measured elements (Zn, Pb, V, Cr, Ni, Cu and B) showed far lower concentrations (1–6 mg/kg), except for Pb and Zn at site 5 (14 and 29 mg/kg). The lowest measured concentrations were found for Co, Sn, As, and Sb (< 1 mg/kg)


Rare Earth Elements
by Geology.com
H
He
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Kr
Rb
Sr
Y
Zr
Nb
Mo
Tc
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Xe
Cs
Ba
La-Lu
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Po
At
Rn
Fr
Ra
Ac-Lr
Rf
Db
Sg
Bh
Hs
Mt
Lanthanides
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Actinides
Ac
Th
Pa
U
Np
Pu
Am
Cm
Bk
Cf
Es
Fm
Md
No
Lr

REE-requiring Products

REEs and bauxite residues

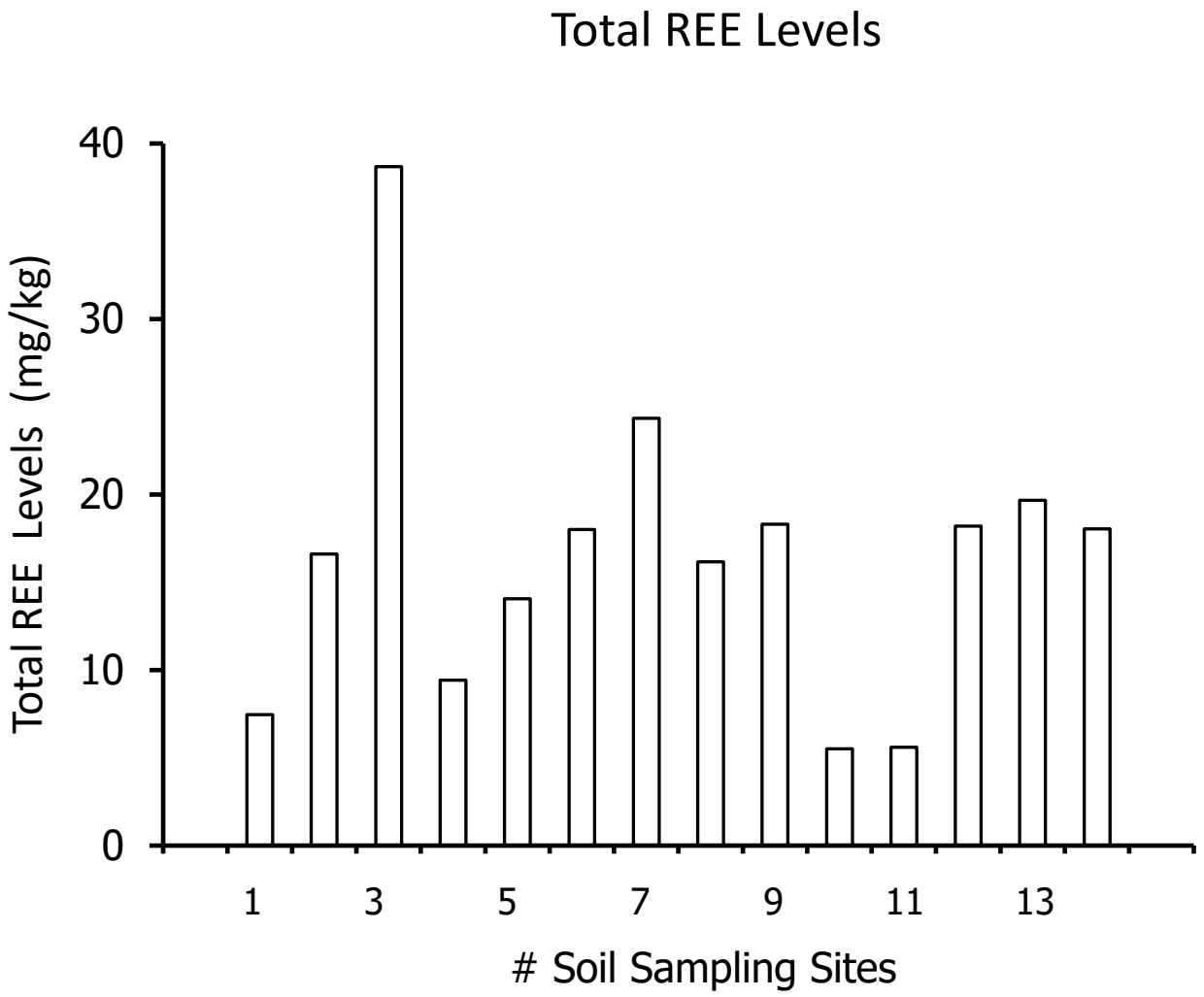
Barros Ó et al. Recovery of rare earth elements from wastewater towards a circular economy. Molecules. 2019 24:1005.

Verma AS et al. Applications of bauxite residue: A mini-review. Waste Manag Res. 2017 35:999-1012.

Liu Y, Naidu R. Hidden values in bauxite residue (red mud): recovery of metals. Waste Manag. 2014 34:2662-73.

Anawati J, Azimi G. Recovery of scandium from Canadian bauxite residue utilizing acid baking followed by water leaching. Waste Manag. 2019 95:549-559.

Rao Borra C et al. Selective recovery of rare earths from bauxite residue by combination of sulfation, roasting and leaching. Minerals Engineering 2016 92:151-159.


Total REE Levels
Total REE Levels (mg/kg)
40
30
20
10
0
1
3
5
7
9
11
13
Soil Sampling Sites

Altogether, both the sea urchin and the nematode bioassay data corroborated the analytical evidence for increased pollution in two distinct areas, close to the BPP and to the PP.

Whether, and if so to what extent, the analytical and bioassay data may raise some concern in terms of environmental and human health, is a sensitive question warranting further investigations in the Gardanne residential and agricultural areas.

Working Hypothesis

Bauxite and its processing sludge display relevant levels of rare earth elements (REEs), as detected in Gardanne soil, where REE levels displayed intermediate values between aluminum & iron, and minor elements, such as Zn, Pb, V, Cr, Ni, Cu and B.

This finding in Gardanne is confirmed by a body of literature.

Working Hypothesis (?)

1. Exploring the REE content in areas previously utilized for red mud lagooning
2. Evaluating safe devices for REE extraction from the lagooning areas

Open Questions

The agricultural areas downwind and downstream *vs*. the Gardanne bauxite-processing facilities have not yet been investigated in our previous studies.
The possible outcomes of *ad hoc* investigations might lead to re-consider the actual influence, if any, of bauxite sludge on local crops and on livestock, which might imply any environmental concern, and require remediation interventions.

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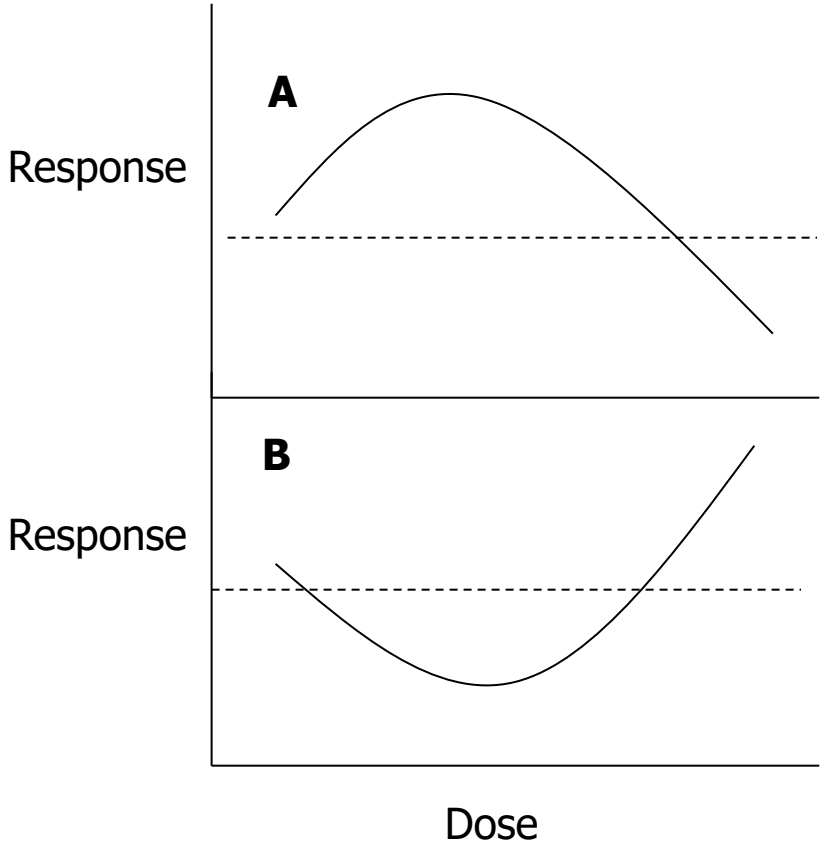
https://doi.org/10.1007/s00244-020-00773-4

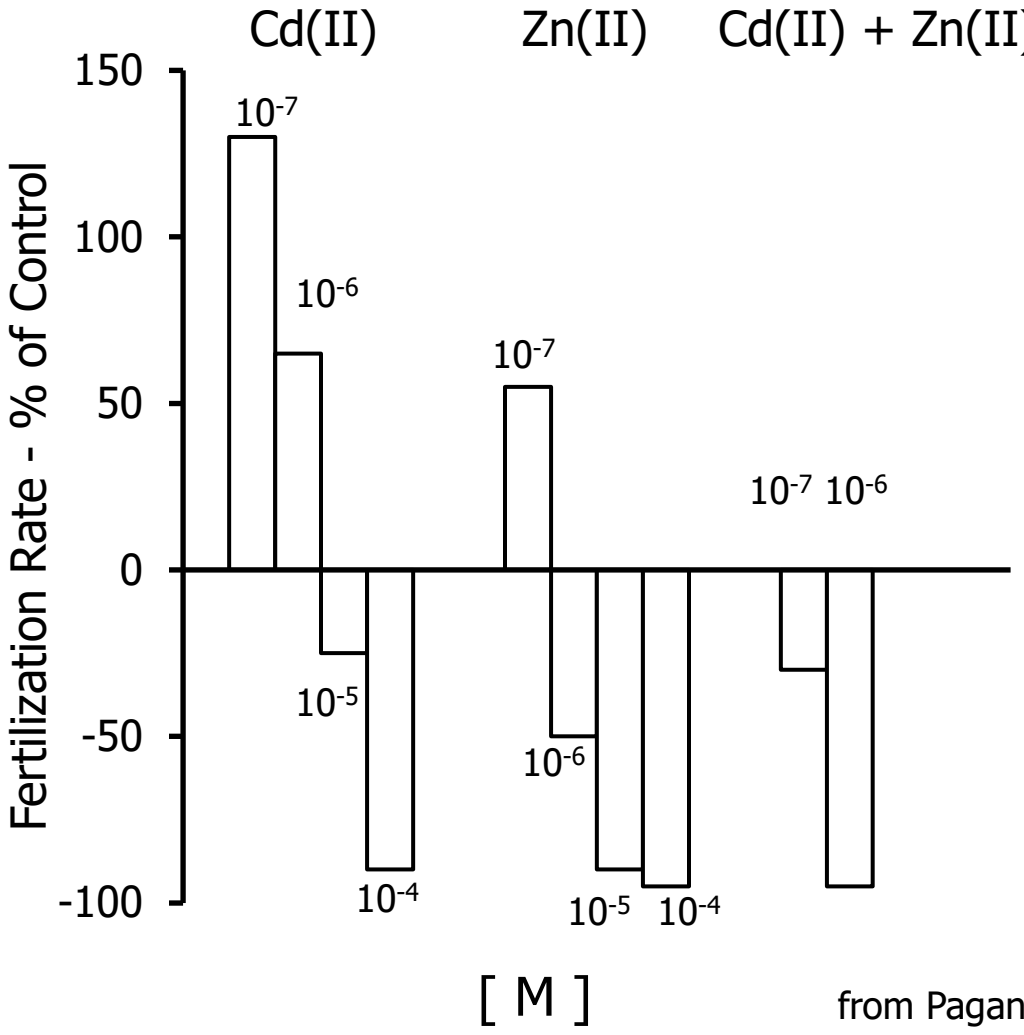
MINI-REVIEW

Review of Rare Earth Elements as Fertilizers and Feed Additives: A Knowledge Gap Analysis

Franca Tommasi[1] · Philippe J. Thomas[2] · Giovanni Pagano[3] · Genevieve A. Perono[4] · Rahime Oral[5] · Daniel M. Lyons[6] · Maria Toscanesi[3] · Marco Trifuoggi[3]

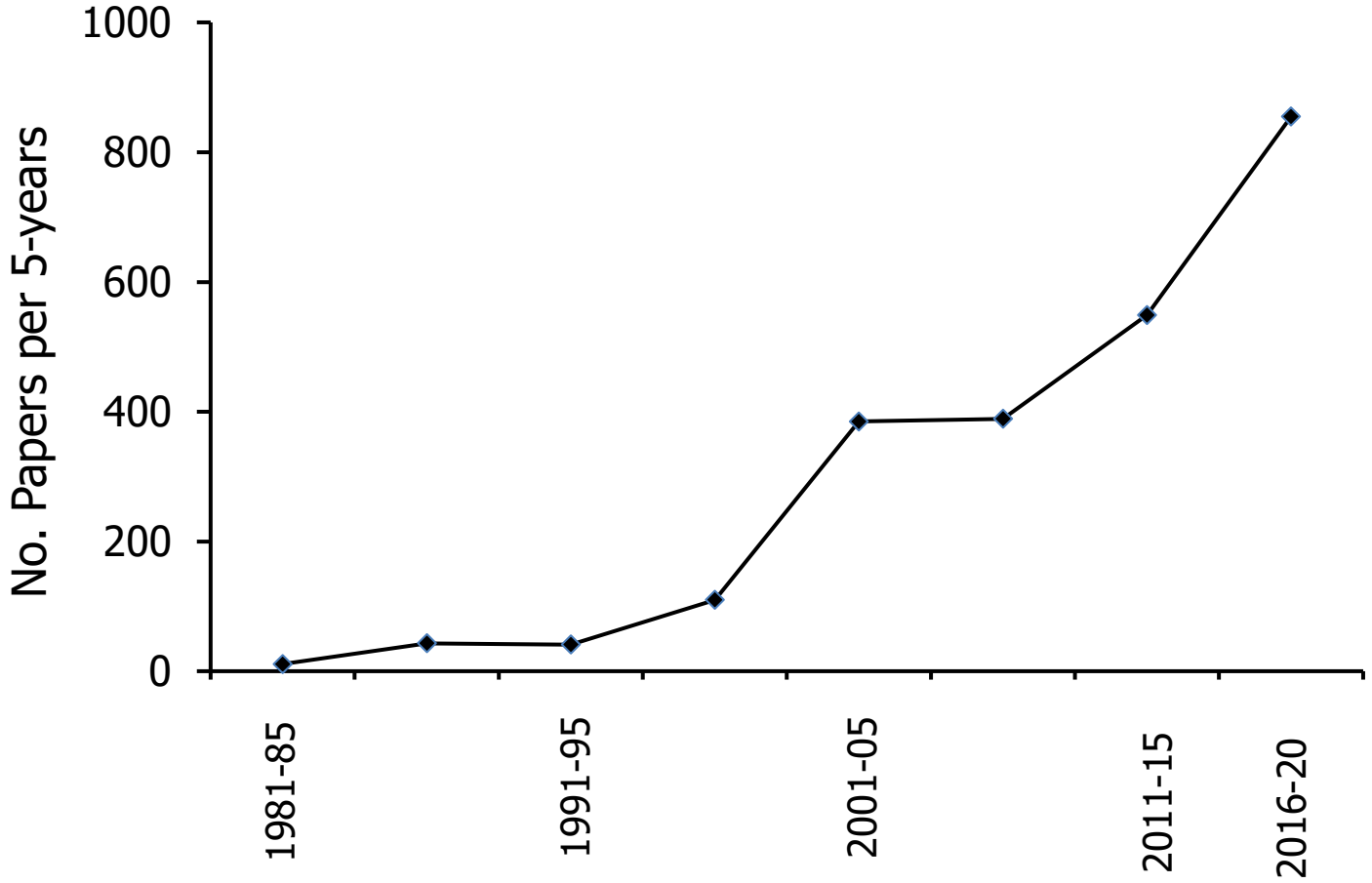
Rare earth elements (REEs) are key constituents of modern technology and play important roles in various chemical and industrial applications. They are also increasingly used in agricultural and zootechnical applications such as fertilizers and as feed additives. Early applications of REEs in agriculture have originated in China over the last several decades with the objective of increasing crop productivity and improving livestock yield (ex: egg production or piglet growth). Outside China, REE agricultural or zootechnical uses are not currently practiced. A number of peer-reviewed manuscripts have evaluated the adverse and the positive effects of some light REEs (lanthanum and cerium salts) or of REE mixtures both in plant growth and in livestock yield. This information was never systematically evaluated from the growing body of scientific literature. The present review aimed at evaluating the available evidence for adverse and/or positive effects of REE exposures in plant and animal biota, and the cellular/molecular evidence for the REE-associated effects. The overall information points to shifts from toxic to favorable effects in plant systems at lower REE concentrations (possibly suggesting hormesis), whereas the available evidence for REE use as feed additives may suggest positive outcomes at certain doses, but requiring further investigations before extending this use for zootechnical purposes.


A
Response
B
Response
Dose



from Pagano et al. (1986)

Hormesis-focused Papers



REE-associated effects in plant models ranged from growth stimulation (hormesis) to inhibitory effects as a function of REE concentration;

Different accumulation gradients were noted in plant and animal organs, with minimal – if any – accumulation in the edible parts;

REE-based feed additives in poultry failed to result in increased weight gain in broiler chicks, whereas REE-supplemented laying hens improved quantitative and qualitative egg production;

Growth performance in REE-supplemented piglets appeared to depend on REE dosages, as increased weight gain was observed for REE dosages >300 mg/kg, and not for a dosage of 200 mg/kg.

MAIN GOAL

Seeking **optimal hormetic effects** of individual vs. combined REEs in plant and animal test models, aimed at inducing the most effective increases in crop yields, as well as the improvement of animal growth.