

REVIEW

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# Chemical indicators for pollution detection in terrestrial and aquatic ecosystems



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## Abstract

**Background:** Pollution is objectionable changes in a given ecosystem trailing to potential health hazards. Assessment of pollution levels is continually recognized by several pollution indicators, biological, chemical, and/or physical. Chemical indicators always validate fair information about the evenness between ecosystem components.

**Results:** Chemical indicators include pH, quality criterion index, kinetics, oxidation-reduction potential, reactive carbon, total organic C, total residues, dissolved oxygen (DO), chemical oxygen demand (COD), biological oxygen demand (BOD), phosphate (P), nitrogen (N<sub>2</sub>), anhydrous ammonia (NH<sub>3</sub>), nitrate (NO<sub>3</sub>), and copper (Cu<sup>2+</sup>).

**Keywords:** Aquatic ecosystems, Chemical indicators, Pollution, Terrestrial ecosystems

## Introduction

There are three main crucial categories of ecosystem pollution indicators: biological, chemical, and physical. Chemical pollution is habitually used to measure how well an ecosystem functions through certain qualitative and quantitative parameters. An ideal pollution indicator should be well correlated with the ecosystem processes, integrated with their properties, manageable to many users, sensitive to changes, and interpretable. Chemical pollution indicators are predominantly linked to nutrient cycling, water relations, and buffering capacity (Hill et al. 2003). European Environment Agency (EEA) elaborated certain pollution indicators to fulfill decisive policy questions validating all components of ecosystem management, starting from setting policy frameworks to calibrate targets and from policy observing and appraisal to communicating to policy-makers and the public in general (El-Ashry et al. 2011). EEA pollution indicators might be classified as descriptive, functioning, efficient, policy, and total well-being indicators (Fernández-Calviño et al. 2017).

The key objectives of pollution indicators seek to comprehend the impacts of human activities on natural ecosystems, justify responsibilities, and maximize the consequence of R&D role (Cuffney et al. 2000). The aim of this work is to beam weightless on the weight of using

chemical pollution indicators for the sake of well managing ecosystem pollution tribulations. Only the most characteristic and dependable indicators with actual practice will be presented.

## Chemical pollution indicators

The quality indicators of terrestrial and aquatic ecosystems are merely chemical measurements able to detect the ecosystem status besides affecting the varied reactions and processes tacking place therein (David and Stephen 2000). Attributes of good chemical pollution indicators include promoting biodiversity, degrading pollutants, controlling the regulation and partition of aquatic and solute flow, cycling carbon and nutrients, and supporting structures associated with human habitats (Fayad et al. 2013; Peterson et al. 2001).

## Acidity

The pH values point to the level of acidity or alkalinity in a given ecosystem. From a chemical point of view, pH is the log<sup>10</sup> of H<sub>2</sub> ions (H<sup>+</sup>) in a given system. The pH scale varies between 0 and 14; a pH of 7 is neutral, greater than 7 is basic or alkaline, and below 7 is acidic. It is worthy to state that because the pH gage is presented in logarithmic units, any minute change in its value might significantly lead to serious changes in most of the chemical characters and some biological processes as well in a given ecosystem. For example, an ecosystem having a pH of 5 is 10 or 100 times more acidic than a

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pH of 6 or 7. Hydrogen ions in the ecosystem solution come from  $\text{CO}_2$  released during organic matter decomposition, root respiration, and the atmosphere. Other sources of  $\text{H}^+$  ions are from root exudates, nitrification process,  $\text{NH}_4$  released from fertilizers, organic matter mineralization sulfur reactions, and fallout particularly acid rain. The resistance of varied ecosystems to any drop or rise in their pH value is linked with their high or low buffering capacity (Smith and Doran 1996). Therefore, the quantity of limestone ( $\text{CaCO}_3$ ) needed to raise pH in an acid ecosystem to a desired value must be solely determined for each ecosystem before amending. The continuous application of acidic fertilizers, such as  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$  and S, to alkaline ecosystems predominantly diminishes their pH values. Also, cultivated leguminous could, however, slightly lower the pH value. Furthermore, it is well known that colloids such as clay, humus, and microorganisms act as buffers resisting pH alterations. The pH values are considered as an excellent chemical pollution indicator which simultaneously affects and responds to the status in any ecosystem. It controls solubility, toxicity, and mobility of most potentially toxic elements (PTEs) and nutrients and influences saturation percentage, buffering capacity, cation exchange capacity (CEC), and most biological characters. Changes in the pH of a given ecosystem significantly impact its character and processes as well as plant growth. The nutrition, growth, and yields of most crops are always diminished under low pH and increased as the pH rises to a proper level. The best growth of many crops was always recorded under a pH close to neutrality (6 to 7.5) although a few crops prefer to be grown under acid or alkaline ecosystems. In acidic ecosystems, Ca, Mg,  $\text{NO}_3$ , P, B, and Mo are deficient, whereas Al and Mn are abundant and sometimes reach a toxic level for some plants. Furthermore, P, Fe, Cu, Zn, and B are frequently deficient in high-alkaline ecosystems. Bacterial populations and their activities are always declined at low pH levels, whereas fungi are altered to an extensive range of pH. Other microorganisms have varied optimum pH ranges for their good survival and function as given in Table 1.

The mobility and decomposition of organic pollutants, e.g., herbicides, insecticides, and the solubility of PTEs are pH dependent. The consequences of ecosystem pH

on cation availability affect aggregate stability since multivalent cations, e.g., calcium ions, perform as links between organic and mineral colloids.

### Ecosystem quality criterion index

Zinc equivalent equation numerically designates the levels of PTE toxicity according to the following equation (ppm): Zn concentration  $\times 1 + \text{Cu}$  concentration  $\times 2 + \text{Ni}$  concentration  $\times 8$ .

A quality criterion index over 200 units indicates a risky situation necessitating remediation for sustainable farming management (USEPA 2000). This model could be used in all polluted ecosystems. It was repeatedly expended as a chemical indicator for ecosystem pollution and as a gage for success of ecosystem remediation. El-Ashry et al. (2011) characterized the chemical properties of Abo-Rawash and El-Gabal El-Asfar sewage farms. They found that the Zn equivalent parameter values were over the critical values and ranged between 137.5 and 563.5 at El-Gabal El-Asfer and between 52.55 and 633.9 at Abu-Rawash farms.

### Kinetic parameters as chemical pollution indicator

The rate constants of kinetic models were calculated and used in several studies as chemical indicators under different pollution conditions. Saber et al. (2014) studied the rate of Zn, Cu, and Ni desorption at El-Gabal El-Asfar and Abou-Rawash sewage farms where irrigation with sewage effluents was practiced for extended periods. They used modified Freundlich model (MFE), the best model under arid and semiarid conditions, and confirmed, in light ecosystem texture under pH ranging between 6.5 and 6.91, a decrease in the rates of constants of MEF under 0.09, 0.11, and  $0.10 \text{ mg kg}^{-1} \text{ h}^{-1}$  which might be temporarily safe. In heavy ecosystem texture at Kafr El-Sheikh soils irrigated with low-quality water composed of industrial, sewage effluents, and agricultural drainage, under a pH value ranging between 7.4 and 7.9, they found a decrease in the rate constants of magnetic field effect (MFE) under 0.11, 0.13, and  $0.12 \text{ mg kg}^{-1} \text{ h}^{-1}$  that could be safe.

### Salinity

Salinity is the total amount of inorganic mineral compositions existing in a given ecosystem. Salinity is a valuable indicator determining the chemical compositions of the water in ecosystems and is also used to assess the applicability of irrigation water from a salinity point of view. It is habitually used in assessing natural water quality as the sum mass of regularly major tested ions. Electrical conductivity had been habitually used as a chemical indicator for ecosystem pollution (Table 2). Electrical conductivity (EC) value had been used also as an alternative measure for organic matter, cation-exchange capacity, texture, thickness, nutrients, water holding capacity, and drainage

**Table 1** Maximum, minimum, and optimum pH values for microorganisms

Microorganism	Range	Optim.	Reference
Bacteria	5–9	7	Rosso et al. 1995
Actinomyc.	6.5–9.5	8	
Fungi	2–7	5	
Blue-green bacteria	6–9	> 7	
Protozoa	5–8	> 7	

**Table 2** Classes of salinity and EC (1 dS/m = 1 mmhos/cm; adapted from NRCS Soil Survey Handbook)

EC (dS/m)	Status	Reference
0 < 2	Non-saline	Watson et al. (2000)
2 < 4	Very slightly saline	
4 < 8	Slightly saline	
8 < 16	Moderately saline	
> 16	Strongly saline	

conditions as well (Smith and Doran 1996). High EC values had always been associated with extreme levels of ecosystem pollutants, besides most microorganisms proved to be delicate to the existence of high salts in their surroundings.

Actinomycetes and fungi, however, are less sensitive to salts compared to bacteria except halophytes. Most microbial activities, involving respiration and nitrification, were always declined as EC values increases. High EC values could act as a chemical indicator for salinity problems in various ecosystems.

Under EC value > 4 dS/m, most biotas are impeded (Tables 2 and 3). Ecosystems with high EC values resulting from high Na concentration are characterized with poor structure and drainage, and Na is toxic to plants. Conductivity is frequently used in the indirect conjecture of the total concentration of ions in any ecosystem. Conductivity of clean water being very low increases in the presence of inorganic acid, alkali, or salt. The conductivity of water solution rely on the nature and concentration of ions, temperature, and viscosity. Any increase in the temperature would cause a raise in conductivity.

### Oxidation-reduction potential (ORP)

The oxidation-reduction potential in soil and water ecosystems is quite complex and contains several oxidation-reduction couples whose oxidation-reduction potentials result from the drop in the number of oxidation and reduction substances. The oxidation-reduction potential is

**Table 3** Relative yield of selected crops grown in a corn, small grain, legumes, or timothy rotation at different pH levels (USDA 2011)

Crop	pH values				
	4.7	5	5.7	6.8	7.5
Corn	0	73	83	100	85
Wheat	68	78	89	100	99
Oats	77	93	99	98	100
Barley	0	23	80	95	100
Alfalfa	2	9	42	100	100
Soybean	65	79	80	100	93
Timothy	31	47	66	100	95

a significant chemical pollution indicator for the migration and transformation of pollutants in water ecosystems (Bradl et al. 2005). The natures of the major solutes depend to a great extent on the type, speed, and balance of water oxidation.

### Reactive carbon

The reactive carbon (RC), organic matter content in a given ecosystem, contains numerous C complexes with varying levels of degradability, from very easy to extremely resistant (recalcitrant). Each C component has a different residence time in the ecosystem and performs different functions. Reactive carbon (RC), recognized as permanganate oxidizable carbon [POXC], is the most readily decomposable carbon by microorganisms, the most easily bound to minerals, and definitely oxidized by potassium permanganate which renders it a chemical and not a biological pollution indicator (Lucas and Weil 2012). Nevertheless, recent research within a range of ecosystems and management conditions confirmed that POXC was significantly related to the particulate organic carbon, ecosystem microbial biomass carbon (BMC), and in some cases organic C. The residence time of RC is determined to be between 2 and 5 years, in contrast to recalcitrant C (e.g., hummus) that has turnover time of many hundreds to thousands of years. RC originates from various segments of organic matter including fresh organic matter, microbial biomass, particulate organic matter, and some other easily metabolized organic compounds, such as carbohydrates (sugars) and proteins (amino acids) together with loosely C bound to ecosystem minerals. Because of its comparatively brief turnover time, RC is more delicate to management alterations influencing C in agro-ecosystems than total organic C (TOC). RC could be applied as a chemical pollution indicator monitoring the changes following cropping, and ecosystem management performs manipulation of their organic matter content. It is worthy to mention that organic matter, or more specifically ecosystem carbon, surpasses all three indicator categories and has the greatest widely recognized influence on ecosystem pollution as it is tied to all ecosystem functions.

Ecosystem C influences some other pollution indicators, such as aggregate stability (physical), nutrient retention and availability (chemical), and nutrient cycling (biological), and by itself is a sign of ecosystem quality.

### Total organic carbon

Total organic carbon (TOC) is a composite chemical pollution indicator for overall organic compounds existing contained in any aquatic ecosystem (Kinniburgh et al. 1999; Weng et al. 2001). As the TOC was estimated by combustion, the entire organic compound materials in an aquatic ecosystem are oxidized; hence, TOC is a direct

chemical indicator compared to either biological oxygen demand (BOD) or chemical oxygen demand (COD) in estimating all organic matters. Therefore, it is regularly used to estimate the degree of organic pollution in any aquatic ecosystem.

### Carbon dioxide

CO<sub>2</sub> found in aquatic ecosystems is mainly in the form of dissolved gas molecules, but a small amount of it might also be combined with water and generates the carbonic acid that bonds with alkaline substances in rocks the sediments. CO<sub>2</sub> has a unique role in the biochemical reactions between water and biotas. The foremost source of CO<sub>2</sub> carbon in the surface water is the degradation of organic matters in the water and sediment as well as water respiration, and it could also be absorbed from the air.

Therefore, its content might be an indirect indicator in any aquatic ecosystem subjected to organic pollution (Hoballah et al. 2017).

### Total residue (TR)

Total residue is the material left in the containers after the evaporation or drying of water or sewage in a certain temperature, including the “unfilterable residue” (all the residues that is stuck in the filter, also identified as suspended solids) and “filterable residue” (all residues that go through the filter, also recognized as soluble solids). Suspended solids might affect the transparency of a given aquatic ecosystem, reduce photosynthesis, restrict normal movement of aquatic biotas, slow underwater activity, cause hypoxic at the bottom of the water ecosystem, and reduce the assimilation capacity of the ecosystems (Jiang et al. 2004). Using total residues as a chemical pollution indicator is recommended by many scientists.

### Dissolved oxygen

Dissolved oxygen [DO] content in a natural aquatic ecosystem is contingent on the balance between aquatic and atmospheric O<sub>2</sub>. Normally, DO in clean surface aquatic ecosystems is close to saturation. The saturation of dissolved oxygen is closely linked with the partial pressure of O<sub>2</sub> in ambient air, atmospheric pressure, water temperature, and organic and inorganic reducing substances. Under extend atmospheric oxygen, DO would gradually decrease even closer to zero. Thus, anaerobic bacteria would breed and the water quality deteriorates, leading to fish mortality. The discharge of a large amount of wastewater in aquatic ecosystems led to increases in ozone-depleting substances and decrease of DO as well. Therefore, DO is an important chemical pollution indicator in aquatic ecosystems (Kalenik 2014).

### Chemical oxygen demand

COD refers to the number of oxidants consumed in the oxidation of water samples in a specified condition. When the pollution degree of restored substances in a given aquatic ecosystem includes organic matter, NO<sub>3</sub>, Fe salts, and sulfide, COD could be used as a chemical pollution indicator particularly for organic pollution. It is worth to state that COD reflects only the oxidation of organic pollutants, not polycyclic aromatic hydrocarbons or dioxin-like compounds. COD of water samples might vary within the types and the concentration of oxidant that has been added, the acidity of the reaction solution, temperature, and time, as well as with the existence or absence of catalysts. Hence, COD might also be regarded as a condition indicator. China uses a potassium dichromate method in testing wastewater; for their COD, permanganate index refers to the amount of potassium permanganate consumed as an oxidant to deal with water samples in acid or alkaline medium (Rafique 2001). Permanganate index is often considered as a comprehensive index of the degree of pollution of the surface aquatic ecosystems by organic pollutants as well as reduction inorganic materials.

### Biochemical oxygen demand

Domestic sewage and industrial wastewater contain a large number of organic pollutants in various forms. In polluted aquatic ecosystems, the decomposition of organic pollutants consumes a lot of dissolved oxygen and thereby disturbs the balance between oxygen compounds, deteriorates water quality, and causes death to fish and other aquatic biotas due to hypoxia. Organic pollutants in aquatic ecosystems are complicated, so it difficult to determine their ingredients one by one. Oxygen consumed by organic compounds in aquatic ecosystems under certain conditions is used indirectly to estimate the content of their organic pollutants, while BOD as a chemical pollutant indicator falls into this category (Ngang and Agbazue 2016).

### Nitrogen

Nitrogen (N<sub>2</sub>) refers to the content of nitrogen estimated by the Kjeldahl method. It mostly contains NH<sub>4</sub>-N, varied organic N compounds mainly proteins, amino acids, nucleic acid, and urea together with many synthetic organic N compounds in a negative trivalent state (Gorman et al. 2017). In most cases, N is the former NH<sub>4</sub> ammonium that exists in aquatic ecosystems. Determination of either organic N or Kjeldahl N aims to know the situation of water pollution. It is a significant chemical pollution indicator in assessing eutrophication in lakes and reservoirs. Discharge of high amounts of domestic sewage, agricultural drainage effluents, or nitrogen-containing industrial effluents into aquatic bodies almost lead to an increase in

organic and inorganic N compounds as well as in biotas that consume DO and lower the water quality. Under the existing high N and P contents in a given aquatic ecosystem, serious phytoplankton reproduction and eutrophication in the aquatic ecosystem are expected. Therefore, total N might be seen as an important chemical pollution indicator assessing water quality.

### Nitrate

Nitrate [ $\text{NO}_3\text{-N}$ ] refers to the intermediates of the N cycle and is unstable. It might be oxidized to  $\text{NO}_3\text{-N}$  or reduced to ammonium ( $\text{NH}_4\text{-N}$ ). It is a form of inorganic N naturally occurring in all aquatic and terrestrial ecosystems.  $\text{NO}_3\text{-N}$  is mostly released from organic residue degradation, compost, chemical fertilizers, root exudates, rainfall, and light. Eventually,  $\text{NO}_3\text{-N}$  ions are immobilized by microorganisms and converted into organic N usually released back to the ecosystem in plant-available forms. In well-drained aquatic and terrestrial ecosystems,  $\text{NH}_4$  and  $\text{NH}_3$  are converted into  $\text{NO}_3$  by *Nitrosomonas* sp. and *Nitrobacter* sp. through nitrification. On the other hand, the de-nitrification process biologically converts  $\text{NO}_3\text{-}$  to  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{N}_2$ . Such a process often goes under anaerobic conditions in wet ecosystems and also under water-logging conditions. Even when nitrifying bacteria are very active in the outer parts of the aggregates in well-aerated ecosystems, denitrification occurs in anaerobic microsites inside the aggregates.  $\text{NO}_3\text{-N}$  is highly soluble in water and is easily lost by runoff and with surface and subsurface water flows and/or moved to groundwater. In aquatic ecosystems, significant differences between  $\text{NO}_3\text{-N}$  contents range from the tens of micrograms per liter to tens of milligrams per liter. While the content of  $\text{NO}_3\text{-N}$  in clean water being very low, it is relatively high in polluted waters and some deep underground waters. The intake of nitrate or nitrite generated by biotas might be poisoning, as when it reaches up to tens of milligrams per liter, it causes poisoning to biotas. Hence,  $\text{NO}_3\text{-N}$  is considered as the main chemical indicator that could measure ecosystem pollution (Jorgensen and Halling-Serenson 2014).

### Anhydrous ammonia

Anhydrous ammonia [ $\text{NH}_3$ ] refers to a chemical combination of ammonia in the form of ammonia or ammonium ions. The composition ratio between these two depends on the pH and the temperature of the water. When the pH value is high, the proportion of free ammonia is higher. On the contrary, when the pH value is low, the proportion of ammonia is lower. The main source of ammonia in water is the decomposition products of nitrogen-containing organic compounds by biotas. In oxygen-free ecosystems, the  $\text{NO}_3\text{-N}$  nitrite existing in water might also be affected by microorganisms and reduced to ammonia. In aerobic ecosystems,

ammonia in water could also turn into  $\text{NO}_3\text{-N}$  and might even further turn into  $\text{NO}_2\text{-N}$ . The estimation of the various forms of  $\text{N}_2$  compounds in aquatic ecosystems contributes to the evaluation of water pollution and its “self-purification” status. Biotas might be very sensitive to  $\text{NH}_4\text{-N}$  in the water. High levels of  $\text{NH}_4\text{-N}$  would lead to biotas’ death. Thus,  $\text{NO}_3\text{-N}$  is considered as the main chemical indicator measuring ecosystem pollution.

### Phosphorus

The content of phosphorus [P] in the Earth’s crust amounts to nearly 1000 ppm (Dahlquist and Hellstrand 2017). It exists in nature in varied forms of phosphates. It is also found in the living cells, bones, and teeth and is vital for humans, plants, and animals. Daily intake of P reaching 0.4 g for adults is mostly supplemented through water and food, yet in inorganic or organic phosphorus compounds, P existing in the ecosystem as a single mass P is expected to be harmful. Yellow P compounds are vital raw chemical material, as it turns into “P poisonous water” that contains great deals of soluble P and suspended-state P elements, leading to excessive harm to the ecosystem. Phosphorus is a highly toxic material that once enters the living biota cells might lead to acute poisoning (Razzaque 2011). The lethal dose for human intake is 1 mg/kg. Therefore, P is considered a pollutant that would not be ignored. In the natural aquatic ecosystems, almost all P exists in various forms usually divided into orthophosphate, condensed phosphates (pyrophosphate, meta-phosphate, and multi-phosphate), and combined organic P (e.g., phospholipids). They mostly exist in solution, humus particles, or aquatic biotas’ cells. P content in natural aquatic ecosystems is not that high, yet it is relatively high in industrial and domestic effluents, smelting, and synthetic detergent industries. Phosphorus is one of the elements necessary for biota growth, but its high content in aquatic ecosystems (in excess of 0.2 mg/l) might result in algal bloom overgrowth when reaching hazardous levels (eutrophication) (Chapman 2003). Under such a marked diminish, the water transparency of lakes and rivers appears together with a noticed deterioration of water quality. For that, P is seen as an important chemical pollution indicator of water.

### Copper

Establishing reference values for copper (Cu) from EDTA and DTPA extractions or EDTA/total and DTPA/total ratios might result in better chemical pollution indicators distinguishing possible terrestrial and aquatic ecosystem risks from Cu that set critical decisions about their remediation strategies (Malizia et al. 2012; Fernández-Calviño et al. 2017). Thus, Saber et al. (2015) recommended that Cu might be used as a chemical pollution indicator

with Ni and Zn through the Zn equivalent parameter; the presence of these pollutants in soil ecosystem enhanced the toxicity of Ni in the soil ecosystem as a synergistic reaction between these pollutants (Saber et al. 2012).

## Conclusion

In this work, the significance of chemical indicators for monitoring soil pollution was documented about two decades ago. A variety of chemical properties have been proposed for monitoring purposes of soil pollution. The importance of particular chemical monitoring could be inferred from the frequency of their use in various national and international programs. It should be mentioned that extensive calibration should be applied under all relevant conditions. The use of even one of the most suitable chemical properties will yield only qualitative information on pollution levels.

## Acknowledgements

This work was supported and funded by the National Research Centre.

## Authors' contributions

MS helped determine the chemical indicators of heavy metals in soil. AZ and CD helped in the relationship between the fates of pollutants in relation to soil properties. MS and AZ wrote the chemical indicators and revised the whole manuscript after it is written by CD and AZ. All authors contributed equally in the all article steps, wrote the paper, and approved the final manuscript.

## Funding

This work was supported and funded by the National Research Centre.

## Availability of data and materials

The datasets generated and/or analyzed during the current study are included in this published.

## Ethics approval and consent to participate

Not applicable.

## Consent for publication

Not applicable.

## Competing interests

The authors declare that they have no competing interests.

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Received: 18 August 2019 Accepted: 24 September 2019

Published online: 15 November 2019

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