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Designing a reliable leak bio-detection system for natural gas pipelines

F.A. Batzias [a], C.G. Siontorou [a,*], P.-M.P. Spanidis [b]

[a] Univ. Piraeus, Dept. Industrial Management & Technology, Karaoli & Dimitriou 80, 18534 Piraeus, Greece
[b] Asprofos Engineering S.A, El. Venizelos 284, 17675 Kallithea, Greece

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ABSTRACT

Monitoring of natural gas (NG) pipelines is an important task for economical/safety operation, loss prevention and environmental protection. Timely and reliable leak detection of gas pipeline, therefore, plays a key role in the overall integrity management for the pipeline system. Owing to the various limitations of the currently available techniques and the surveillance area that needs to be covered, the research on new detector systems is still thriving. Biosensors are worldwide considered as a niche technology in the environmental market, since they afford the desired detector capabilities at low cost, provided they have been properly designed/developed and rationally placed/networked/maintained by the aid of operational research techniques. This paper addresses NG leakage surveillance through a robust cooperative/synergistic scheme between biosensors and conventional detector systems; the network is validated *in situ* and optimized in order to provide reliable information at the required granularity level. The proposed scheme is substantiated through a knowledge based approach and relies on Fuzzy Multicriteria Analysis (FMCA), for selecting the best biosensor design that suits both, the target analyte and the operational micro-environment. This approach is illustrated in the design of leak surveying over a pipeline network in Greece.

1. Introduction

Pipelines are seen as one of the most practical and economically effective modes for transporting large volumes of flammable and potentially dangerous substances, such as natural gas (NG), for which road or rail transportation is often impractical [1]. In most countries, the more the pipeline systems are expanded and NG consumption increases, the more their economies become dependent on the stable, continuous and safe operation of these facilities [2]. The EU has effective energy relationships with traditional NG suppliers from inside the European Economic Area, notably Norway and The Netherlands, and outside, Russia, Algeria and Central Asia countries, utilizing approximately 200,000 km of offshore and onshore/inland pipelines in order to serve 90 million customers [3]; as the EU import dependence is expected to increase from 57% today to 84% by 2030 [4], 40,000 km of new pipelines are currently under construction [5]: the North European gas pipeline, the Baltic gas interconnector, the Algeria-Northern Europe connection, the Turkey-Greece interconnector, the Greece-Italy interconnector, the Nabucco gas pipeline, and the East Mediterranean gas ring.

Systematic leakage of NG from transporting/storing facilities is common although not directly observable, since it is odorless (odorant is added for easy detection when transported/distributed in cities through the low pressure network), colorless and immediately diffusible. Moreover, according to international historical data (e.g., see [6–8]), accidents involving natural gas pipelines do happen, even though the frequency of such occurrences is generally low compared to road or rail accidents. The major contributors to accidental events in NG pipelines are [9]: external interference, erosion, mechanical failures and construction defects, earth movement and natural disasters, and other unknown causes. Pipeline leakage often results in consequences which have impacts of different dimensions. NG releases from ruptures or punctures in pipelines can cause fatalities, large economic losses and environmental damage [10,11]. Due to the combustible, explosive and diffusible nature of NG and its constituents (as hydrogen sulfide, mercaptans, etc.), its systematic or accidental release into the atmosphere creates a dangerous situation that may provoke explosions and fires [12]. Health concerns regarding chronic exposure include offspring sex ratio at birth of families [13], haematological changes [14] and alteration of blood pressure of individuals resident in long-term contaminated areas [15].

Concerns have been also raised about the contribution of methane leakages to the greenhouse effect. The infrared absorption of one molecule of CH_4 circulating in the current atmosphere is 32 times as large as the infrared absorption of one CO_2 molecule. Several authors have suggested that a few percent leakage of natural gas would offset the advantage of its lower CO_2 emission, when used as fuel [16–18]. Atmospheric CH_4 is mainly consumed

* Corresponding author. Tel.: +30 2104142368; fax: +30 2104142392.
E-mail addresses: fbatzi@unipi.gr (F.A. Batzias), csiontor@unipi.gr (C.G. Siontorou), pspani@asprofos.gr (P.-M.P. Spanidis).

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Table 1
Pipeline detection systems.

On-line leak detection systems	Examples
Techniques without permanent instrumentation on the line Generally, these techniques allow detection and localization of large leaks. They do not permit permanent supervision of the line	• Visual inspection of the line (by the line operator or unofficially by people living nearby) • Airborne visual inspection • Airborne infra-red inspection • External detection of the sonic or ultrasonic noise generated by a leakage in a subsea or underground pipeline • Internal detection of the noise generated by a leakage using instrumented pigs • Detection of a tracer (generally an odourant) added to the fluid
Permanent sensing lines placed along the pipe These techniques, allowing permanent monitoring of the pipeline, can detect and localize small leaks. However, a delay of several hours is often necessary before detection.	• Oil soluble wire whose electrical impedance changes in the case of a leak • Oil soluble tube whose internal pressure decreases in the case of a leak • Oil permeable tube whose gas content is pumped and analyzed at regular intervals • Sensor cable equipped with thermistors to detect variations of the temperature profile due to a leak
Techniques using permanent instrumentation implemented on the pipeline	*Acoustic methods* • Intercorrelation analysis of pressure measurements at two opposite points of a pipe in order to detect the noise created by the leak • System identification with the use of random binary signal excitation *Methods using pressure measurements* • Sudden pressure fall detection in the case of a line break • Detection of a slight pressure decrease or a slight change in the hydraulic profile using time-series analysis • Detection of the negative pressure wave generated by the sudden occurrence of a leak *Methods using flow rate measurements* • Detection of sudden flow rate changes or flow reversal in the case of a line break • Detection of a discrepancy between inlet and outlet flow rate measurements over a predefined time interval *Methods using flow rate and pressure measurements* • All these methods rely on a mass balance

by chemical reactions, mostly with hydroxyl radicals. The increase in CH_4 levels decreases the concentration of hydroxyl moieties and thus lengthens the lifetime of CH_4 in the atmosphere [19], which further increases the importance of methane as a greenhouse gas by establishing a primary deterministic positive feedback loop. In addition, ozone accumulates, which, together with the carbon monoxide produced within the same methane degradation procedure, contributes to increased probability of photochemical smog appearance [20], thus establishing a secondary stochastic positive feedback loop. Although certain non-methane hydrocarbons may be more reactive/efficient in producing photochemical smog contributors/precursors, methane is the most important one since it may appear locally in high concentrations (due to leakage) and propagate in relatively long distance under appropriate micro-climatic conditions. The plumes that are formed by leaks can appear quite differently depending upon the soil characteristics where the pipeline is buried. The voids and porosity of the ground can result in point source or distributed source features at the surface, and the location of the source can be shifted several meters from the actual location of the leak. The situation is worse when the pipeline is uncovered, since the plume is freely created and spread, while the pipeline is mostly susceptible to third party intervention or even terrorist attacks [2,7]. Plumes from pipeline leaks may occur at various leak rates ranging from 0.03 to 300 m^3/h [16,17], depending on the atmospheric conditions. For example, according to routine measurements of atmospheric methane at the station of Lambedousa in the Mediterranean Sea [21], the air masses form northern Algeria display the largest concentrations of methane, most likely because of emissions from NG and oil production and leakage from the NG pipelines.

As evident, ensuring reliable and timely leak detection of the pipeline network is indispensable for the energy sector, posing however many problems due to (a) the vast length of the pipelines, frequently buried underground and necessarily routed through residential populations [6], that raises monitoring costs considerably, and (b) the transboundary infrastructure created that requires bilateral/multilateral agreements for implementing a long-term air monitoring scheme [2]. These requirements have inspirited the development of various monitoring systems (Table 1), like eddy current inspection [22], ultrasonic inspection [23], acoustic method [24], etc., some of them even applied with advanced techniques, such as robotics. Most of these techniques and practices aim at detecting pipeline defects routinely in order to prevent leakage initiation, but they cannot provide for third party interference, which is by far the main cause of leaks in certain regions [9], or seismic activity.

Leak surveying *per se* is based on the detection, preferably identification and (semi-)quantitation, of one of the NG constituents. The typical composition of gas is about 96% methane, 3% ethane and 1% additives/odorizers/tracers, as tetrahydrothiophene, mercaptans, sulfur hexafluoride, and dimethyl ether. Most detection strategies involve methane provided that its background atmospheric concentration is below 2 ppm; background values, however, can vary by up to an order of magnitude when local sources of animal feedlots and active swamp-gas sources are considered [25]. The ethane levels may vary by one percent or two in the pipeline concentrations, but the background sources of ethane are insignificant; accuracy and reliability, however, of measurements at these low concentration levels cannot be guaranteed. Much effort has been expended in the development of technologies to monitor hydrogen sulfide [26–29] but little attention has been paid to other reduced sulfur components as mercaptans. Such measurements can be quite problematic due to selectivity issues and the inherent reactivity of the reduced sulfur functionality where delays in sampling can lead to significant degradation in the more reactive moieties.

The technologies currently available for leak surveying can be broadly classified into non-optical and optical methods: the former include acoustic monitoring [27,28], gas sampling [29], soil monitoring [30], flow monitoring [31,32], and software based dynamic modeling [33,34]; the latter include tunable diode laser spectroscopy (TDLS) [35], laser induced fluorescence (LIF) [36], coherent anti-raman spectroscopy (CARS) [37], Fourier transform infrared spectroscopy (FT-IR) [38], and evanescent sensing [39]. None of these techniques, however, has become the industry standard due to the various limitations involved (Table 2) as well as

Table 2
Comparison of conventional natural gas leak detection techniques.

Technique	Feature	Advantages	Disadvantages
Acoustic sensors	Detects leaks based on acoustic emission	Portable, location identified, continuous monitor	High cost, prone to false alarms, not suitable for small leaks
Gas sampling	Flame ionization detector used to detect natural gas	No false alarms, very sensitive, portable	Time consuming, expensive, labor intensive
Soil monitoring	Detects tracer chemicals added to gas pipelines	Very sensitive, no false alarms, portable	Needs chemicals and thus expensive, time consuming
Flow monitoring	Monitors either pressure change or mass flow	Low cost, continuous monitor, well developed	Prone to false alarms, unable to pinpoint leaks
Dynamic modeling	Monitored flow parameters modeled	Portable, continuous monitor	Prone to false alarms, expensive
Lidar adsorption	Absorption of a pulsed laser monitored in the infrared	Remote monitoring, sensitive, portable	Expensive, alignment difficult, short system lifetime
Diode laser absorption	Absorption of diode lasers monitored	Remote monitoring, portable, long range	Prone to false alarms, expensive, short system lifetime
Broad band absorption	Absorption of broad band lamps monitored	Portable, remote monitoring, long range	Prone to false alarms, short system lifetime
Evanescent sensing	Monitors changes in buried optical fiber	Long lengths can be monitored easily	Prone to false alarms, expensive
Millimeter wave radar systems	Radar signature obtained above pipelines	Remote monitoring, portable	Expensive
Backscatter imaging	Natural gas illuminated with CO_2 laser	Remote monitoring, portable	Expensive
Thermal imaging	Passive monitoring of thermal gradients	Portable, remote sensing	Expensive, required temperature difference
Multi-spectral imaging	Passive monitoring using multi-wavelength infrared imaging	Portable, remote monitoring, multiple platform choices	Expensive, difficult data interpretation

the background conditions prevailing on site. Briefly, the non-optical methods are not specific and the sampling probe must be embedded within the gas plume, as they cannot detect very low concentrations; optical methods, on the other hand, offer the required specificity and sensitivity, but they exhibit the problem of background reflectance: green grass, coarse snow, frost and sandy soil are the least reflective of common background materials. Their use in a domestic or industrial environment could produce false alarms, for example, in the presence of ethanol vapors, or propane, which are the main interfering gases [40,41].

Notwithstanding, detecting leaks in a pipeline network may not be the most difficult task for a leak detection system; detecting leaks without giving false alarms is the main challenge. Concepts like reliability and sensitivity should be especially re-defined and clarified for *ad hoc* usage. Reliability is defined as a measure of the ability of a leak detection system to render accurate decisions about the possible existence of a leak on the pipeline, while operating within an envelope established by the leak detection system design [42]. It follows that the reliability is defined as a function of the probability of detecting a leak, given that no leak has occurred: a system is considered to be more reliable if that probability is low, i.e., if it consistently detects actual leaks without generating incorrect declarations. Sensitivity is a composite measure of the size of a leak that a system is capable of detecting, and the time required for the system to issue an alarm in the event that a leak of that size has occurred.

High selectivity, specificity and sensitivity in ms response times can be achieved by utilizing biosensor technology, which combines natural recognition mechanisms (bioelements or biological systems) with chemical transducers [43,44]. In principle, the high selectivity of the device, presented inherently by the bioelement that is tailored-made to meet the specific analyte(s), excludes most interference problems and matrix effects. Furthermore, the versatility of this technology allows for experimenting with numerous combinations of arrayed bioelements and transducers as micro-detectors in order to detect multi-analyte levels and exclude interference and cross-reactivity; in theory, and to certain extent has been proven in practice [45,46], any bioelement can be coupled with any transducer, allowing for in-built device characteristics to meet any specification requirements or restrictions. Biosensors are worldwide considered as a niche technology in the environmental market, since they afford the desired detector capabilities at low cost, provided they have been properly designed/developed/customized/utilized and rationally placed/networked/maintained/replaced by the aid of operational research techniques [47–49]. Notwithstanding, biosensor technology bears the inherent peculiarity of precluding conventional standardization, since design, fabrication and implementation are almost entirely target-oriented on the basis of the intended operational environment [49].

This paper addresses NG leakage surveillance through a robust cooperative/synergistic scheme between biosensors and conventional detector systems; the network is validated *in situ* and optimized in order to provide reliable information at the required granularity level. Thus, biosensors' lack for standardization procedures/practices is successfully overcome, while the reliability of the pipeline leak monitoring scheme is increased without using redundant sensor networks. The most decisive factor pertaining to the success of the scheme lies within the computer aided biosensor design substantiated through a knowledge based approach and relying on Multicriteria Analysis (MCA), based on fuzzy reasoning to count for uncertainty, for selecting the best bioelement–transducer combination fulfilling the desired specification restrictions referring to the scientific, the engineering and the marketing aspects of the devices. Candidate biosensor structures may come from different stages of development, ranging from already marketed products to bench-scale set-ups; the use of MCA potentially leads to reality-closer and efficient retrieval of alternatives that represent better the technology throughput and is most suitable for utilizing the local capabilities and resources. This approach is illustrated in the case of leak surveying over a high pressure pipeline, involving methane, mercaptans and hydrogen sulfide detection. The formalism adopted is quite flexible to allow for handling a wide range of different cases within the highly demanding and public-sensitive safety prioritization in the energy sector.

2. Methodology

2.1. Overview of the methodological framework

The methodological framework designed/developed by the authors under the form of an algorithmic procedure for computer-aided biosensor design for detection of NG leakage, includes the following 23 activity stages and 7 decision nodes, interconnected as shown in Fig. 1.

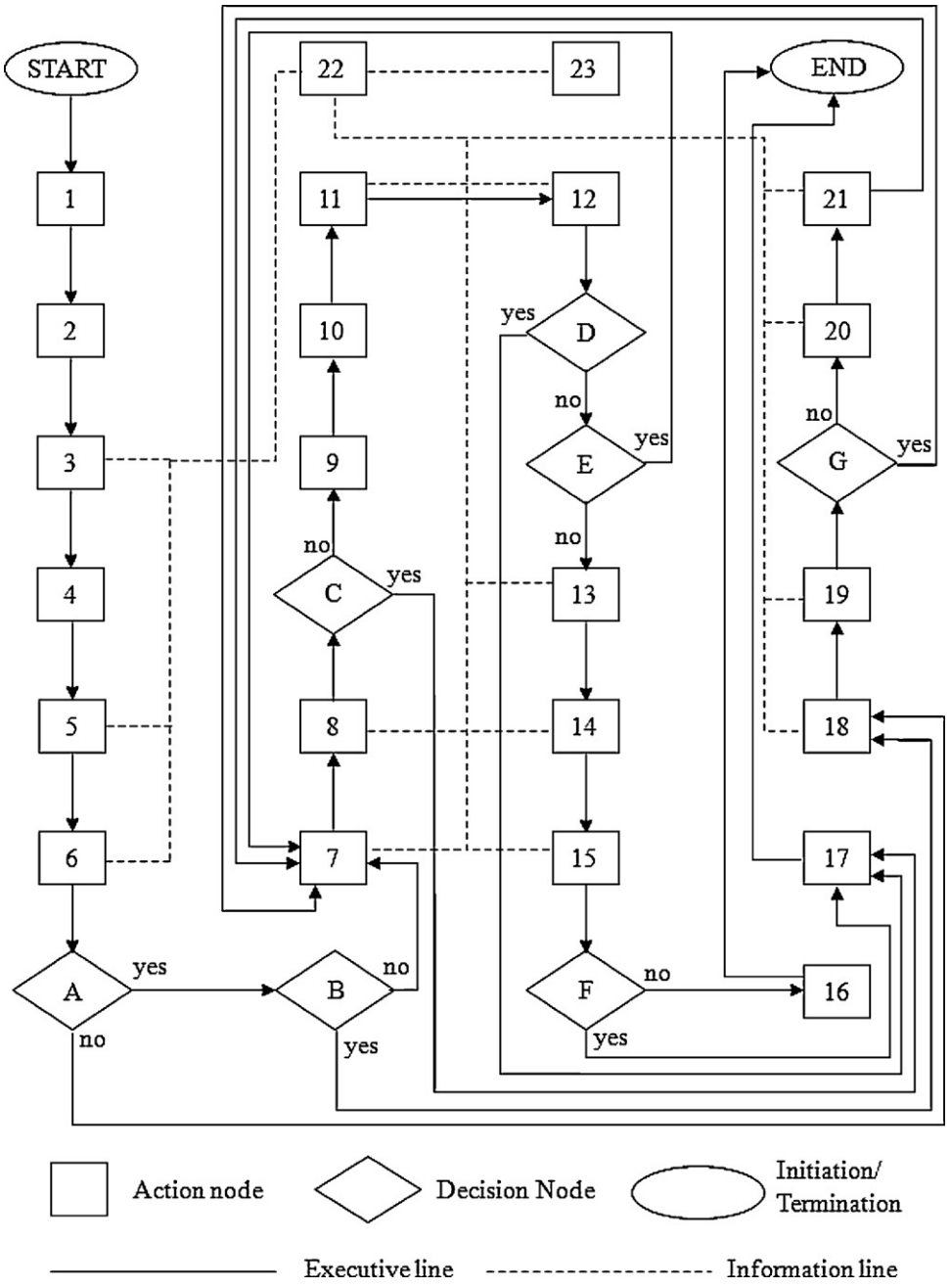

Fig. 1. The methodological framework designed/developed herein under the form of an algorithmic procedure for computer aided biosensor design intended for detection of natural gas leakage during transporting/storing/processing.

1. Determination of composition and characteristic parameter values of the NG.
2. Mapping the pipeline network, the storing facilities, and the processing units on corresponding layers of a Geographical Information System (GIS).
3. Registration of critical characteristics (e.g., sensitive ecosystems, human population density, production activities) on corresponding GIS layers.
4. Risk analysis and expected spatial distribution of environmental impact.
5. Mapping of environmental parameter values to be used as upper limits.
6. Registration of characteristic control variables of the monitoring system in operation, including the conventional techniques used for measuring NG constituents to investigate possible leakage.
7. Collection/categorization of original or slightly modified biosensors capable to measure the constituent/tracer, playing the role of analyte (taxonomy function).
8. Multicriteria choice of the most appropriate original or (slightly) modified biosensor.
9. Decomposition of collected biosensors into distinct parts and enrichment of the new collection with similar parts coming from external Bases (partonomy function).
10. Recomposition to form a new set of biosensors, possibly more capable for measuring the analyte.
11. Multicriteria choice of the most appropriate recomposed biosensor.
12. Testing of proposed biosensor to check its functionality.
13. Selection of the most detectable main NG constituent.

14. Collection of conventional techniques and biosensors appropriate to measure this constituent under weak leakage conditions (worst case reasoning).
15. Multicriteria choice of the most appropriate measuring device.
16. Retention of the initial conventional technique, with the possibility of operating the proposed (in stage 12) biosensor in parallel for improving its functionality through design of experiments *in situ*.
17. Replacement of the initial conventional technique.
18. Collection of substances/additives with proper characteristics to serve as tracers, the constituent already in use (if there is one) included.
19. Multicriteria choice of the most appropriate substance.
20. Collection of conventional techniques suitable for measuring this substance/analyte.
21. Multicriteria choice of the most appropriate conventional technique.
22. Creation/operation/enrichment/updating of a knowledge base (KB).
23. Searching within external bases by means of an intelligent agent (IA) [50].
    A. Is there already a NG constituent, which can be used as a tracer for leakage detection?
    B. Is there a possibility of changing the tracer?
    C. Is the suggested biosensor more satisfactory in comparison with the corresponding conventional technique?
    D. Is the proposed biosensor more efficient, according to tests carried out in stage 12?
    E. Is there another NG constituent, which might serve as a tracer?
    F. Is this device satisfactory?
    G. Is it already in use?

The criteria used in stages 8, 11 and 15 (where the alternatives are biosensors ready-to-use, recomposed biosensors or measuring devices, respectively) are cost (f_1), selectivity (f_2), sensitivity (f_3), resistance to interference (f_4), precision (f_5), reliability (f_6), response time (f_7), and signal-to-noise ratio (f_8), although their weights in the corresponding vector, as well as the set of alternatives in the preference matrix, are completely different. It is worthwhile noting that when the alternatives are not ready-to-use devices but measuring systems still in R&D, the selection criteria of stage 11 should rather address directly the uncertainty (and related development costs) involved in the experimental set-ups [51] rather than focusing on operational characteristics (which, in this case, would be available only at stage 15, i.e., after completing successfully the validation at stage 12). This set of criteria includes: availability of relevant knowledge background, proper equipment and human resources at R&D level, h_1; estimated R&D expenditure for successful completion of the project, h_2; theoretical basis of the physicochemical interaction between analyte and bioelement, especially when an additional interface is introduced between them to improve certain metrological parameter-values (detection range, detection limit, reproducibility, accuracy, precision, specificity), in order to conform to the specifications set at stage 5 and the relevant legislation/norms, h_3; maturity of relevant know-how and diffusion extent of the corresponding technology, h_4; operational life time, especially of the sensing element, in terms of the stability of the biochemical complex and the required/proposed maintenance/(re)calibration protocol (i.e., method, frequency, online/offline testing), h_5; ruggedness of the device, taken into consideration (i) the field environmental conditions under which the device should operate (temperature, wind, rainfall, humidity, extreme weather conditions), and (ii) the sample parameters, especially at extreme ranges of pressure, pH, temperature, concentrations, h_6; prospects for further development, based on applying either (i) breakthrough physicochemical combination (discontinuous innovative action) or (ii) gradual improvement (continuous innovative action) by assuming the biosensor under experimental design to follow a development path similar to some other measuring equipment already successfully tested at a more advanced level, h_7. The use of different sets of criteria for different knowledge layers, i.e., marketing devices (surface layer) and experimental set-ups (deeper layer), helps substantially decision making at different scope and information granularity level. Seemingly, the procedure of decision making is decomposed into a hierarchy of elements influencing the system by incorporating levels referring to objectives, criteria, sub-criteria [49]. In quantitative aspects, the framework proposed can prioritize a set of attributes and distinguish the more important factors for each level.

The criteria used in stage 19 (where the alternatives are candidate tracers) are olfactory threshold (g_1), toxicity (g_2), neutrality in respect to NG constituents and pipeline/tank walls (g_3), environmental friendliness (g_4), cost (g_5), availability (g_6), resistance to decomposition under the conditions most likely to prevail (g_7). The KB of stage 22 is structured by means of a controlled vocabulary [47,48] that ensures an ontological approach in order to avoid misinterpretation of information and misunderstanding between the experts participating in the assignment of (i) weights to the elements of the criteria vector and (ii) grades to the preference matrix, by means of a 3-rounds modified Delphi method.

2.2. The knowledge base

The knowledge base (KB) contains the processed and organized information of biosensor devices, either marketed, prototype or experimental set-ups; it is segmented into four layers. The KB created is linked to the computer-aided selection tool (Fig. 2), by means of an interface that allows the coupling of the four layers with the information retrieval mechanism through a variety of filters that assists in sieving the stored data. The first layer (surface knowledge layer) contains information on the device, seen as a 'black box' that produces measurements: device description, intended use (laboratory, field, online, off-line, etc.), analytical specifications (target analytes, concentration range, interference, calibration, etc.), operational characteristics, maintenance, storage, power requirements, software/hardware, etc. Engineering information is included in the second layer along with quality assurance and quality control tasks and specifications, manufacturing ruggedness (i.e., the use/compatibility of alternative materials for manufacturing), sub-units or auxiliary units (e.g., samplers, signal processing units, etc.), device assembly, and re-engineering/re-processing protocols. As obvious, the first two layers are mostly confined to marketed devices (as the Raptor Plus and the BioHawk), or advanced prototypes (as the biosniffer for methyl mercaptan [52]).

The fourth layer (deeper knowledge layer) processes the information on devices or experimental set-ups and basic biochemical/transduction models, following a decomposition/recomposition procedure, taken also advantage of the information obtained from the third layer (described subsequently, since it constitutes a completely different but nevertheless indispensable/supplementary approach). Each biosensor is decomposed into functional parts; the degree and extent of decomposition depends on the judgment of the expert and the specific needs of the decision-making process for analytical details, depth of knowledge and amount/granularity of information. For example, a biosensor can be decomposed into three parts: the target analyte, the molecular recognition system, i.e., the biological/biomimic element that interacts with

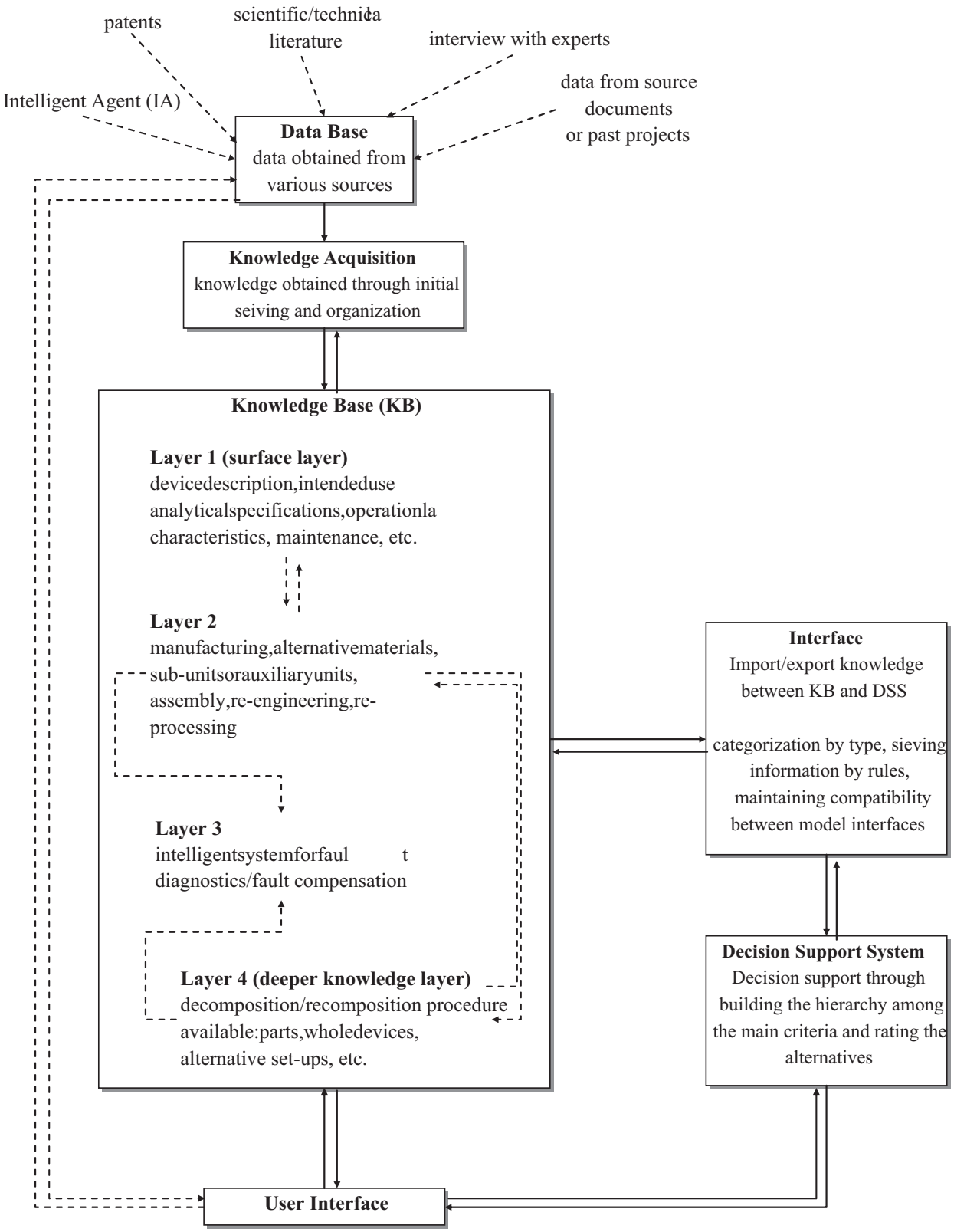

Fig. 2. Schematic overview of the knowledge base designed by the authors for computer-aided selection of bioelement–transducer interface with a view to develop tailored-made devices with in-built analytical and operational optimization.

the target analyte, and the physicochemical transducer that detects the interaction and converts it to an electronic signal [47,48]; however, a more detailed structural and operational decomposition may be required, involving, also, the mechanism of signal generation, the biological/biomimic element/transducer interface, the signal amplification process, the sample pretreatment unit, etc. Upon recomposition, the parts are re-assembled and their inter- and intra-relations are registered; re-assembly

follows a more loose pattern, so that both, the whole device or device parts are readily available for further processing or retrieval.

The decomposition module allows for the selection of alternatives in each part, i.e., alternative biochemical models or transducers, that, in case the compatibility is satisfactory, give rise to improved or entirely new devices in stages 9–10 of the algorithmic procedure. The biosensors reported in literature are usually generic and extremely versatile, since one transducer system can be linked to a variety of bioelements for the detection of the corresponding target analytes [43,44]. Therefore, one biosensor concept can lead to a number of devices and to a wide range of analytes. The specific information contained in this layer prerequisites an extensive literature search for retrieving the chemical/biochemical/electronic inter-/intra relationships, as well as for defining/setting compatibility criteria in order to ensure operation at acceptable efficiency and efficacy. Although conceptual combinations and allocations can be made, it is strongly recommended to rely on some kind of reported testing (even partial) before simulated models are produced.

Nevertheless, selection procedures reliant upon recomposed biosensor designs must be wary of the risks involved, especially at the feasibility of developing a field device. Apart from ascertaining reliability of measurements under conditions of uncertainty as regards fouling, interferences, abrupt background load increases, pressure changes, etc. [47,48], various environmental parameters should be also taken into consideration, as temperature, humidity and extreme weather conditions (frost, thaw, flood, draught). For example, although seasonal temperature changes may be partly compensated by packaging, temperature changes (abrupt fluctuations, in particular) is the main issue, as they may induce surface energy on the adsorption layer [53], alter the kinetics in DNA hybridization [54], change the configuration of adsorbed molecules [55] and cause significant signal deviation in measurement [47]. Numerous compensation methods have been proposed, such as the temperature-dependent current source [56], double-bridge design [57], the linear voltage excitation [58], bias current generator [59], and voltage-to-time converter [60]. Taken also into consideration the fabrication limitations in biosensor [48], development of simple, reliable signal conditioning is necessary.

Such schemes are stored in the third layer which describes fault routes, ultimate error causes, error propagation, and remedial activities. Based on fault tree analysis, this layer provides all events or combination of events that can potential lead to device misfunctions, as noisy signals, dead sensor, etc. [47,48]. Depending on the available information, this layer either draws upon the first layer, in case the devices are already accompanied by an expert system for fault diagnostics (relying on acceptable standard procedures and protocols), or utilizes the information on the fourth layer in order to yield misfunction simulation models from the inter-/intra-relations between the device parts. Such data, however, are scarce in literature; an expert system for fault diagnostics relying on fuzzy reasoning to count for uncertainty, has been recently published by the authors and can be used to offer technical support to biosensor designers/manufacturers to compensate for the lack of standard quality practices [47].

The devices registered in the KB and processed through the multi-layer platform, follow a hierarchical taxonomy based on functional component and operational structure decomposition that provide multiple indices to the decision support tool and enable structured case management. As the number of input devices increases, effective classification is essential. Categorization and hierarchical order (taxonomy function) was developed mainly on the basis of the fourth layer decomposition module. The functional hierarchy is oriented towards supporting cross-domain combination of parts (partonomy function) in yielding alternative designs, whereas the operational hierarchy has been developed to identify common analytes that may be detected, directly or indirectly (e.g., as an interferent) by different biosensor set-ups. For example, the search for a device that measures methane, will retrieve all the dedicated methane devices, all the biochemical models that accommodate methane-related substances and all the devices/set-ups that are interfered by the presence of methane. This hierarchical structure supports the development of efficient domain-specific query mechanisms. The development of the current KB has been focused on representational issues and detailed analysis to support retrieval and composition, rather than minimizing computational capacity requirements and improving efficiency.

2.3. Fuzzy MultiCriteria Analysis

Fuzzy Multicriteria Analysis (FMCA), applied at stages 8, 11, 15, 19 and 21, is used to provide robust selection of biosensors, conventional detectors and detecting substances. The objective function of the multicriteria problem under consideration is $\mathrm{Max}\{f1(a),\ldots, fK(a) \mid a \in A\}$ where A is the set of T alternatives and fk, $k = 1, \ldots, K$, are the K criteria used for evaluation of each alternative. The computational procedure consists of two main steps: (i) the formulation of the preference matrix ($K \times T$), where each element xkt is the evaluation of alternative At according to criterion fk, (ii) the ranking of the alternatives, as a result of applying to the rules of the selected MCA method. PROMETHEE [61] has been used as an outranking method, in its fuzzy version to count for uncertainty [62,63], allowing for incomparability (aRb) and weak preference (aQb) between the alternatives a, b, in addition to the strict preference (aPb) and indifference (aIb) that the 'classical' methods are based on. The notion of a generalized criterion is used to construct an outranking relation by defining the preference index $\Pi(a,b) = \Sigma wiPi(a,b)/\Sigma wi$ as the weighted average of the preference functions Pi, that quantifies the preference of the decision maker of alternative a over b, taking into consideration all the criteria. In terms of topology, the preference index values can be represented as a valued outranking graph, the nodes of which are the alternatives. By summing the column elements in each row of the outranking relation matrix, the flow leaving each node is obtained, which shows its outranking character, while by summing the row elements in each column, the entering flow is obtained for each alternative, which shows its outranked character. By considering the leaving and entering flows, as well as the fact that the higher the leaving flow and the lower the entering flow the better the alternative, the partial preorder (PROMETHEE I) is obtained. Although the partial preorder carries more realistic information, sometimes the total preorder (PROMETHEE II) is requested to avoid any incomparabilities; this preorder is induced by the net flows, i.e., the difference between the leaving and the entering flows. The generalized criterion used is a piecewise linear preference function $P = H(d) \in [0,1]$, where d is the difference of the evaluation of two alternatives a, b. The parameters of $H(d)$ are an indifference threshold q, the greatest value of d below which there is indifference, and a preference threshold p, the lowest value of d above which there is strict preference – the interval between q and p can be considered as the weak preference region.

To conclude a partial or complete preorder from the resulting fuzzy sets, the Tseng and Klein [64] method was used which makes pairwise comparison of the alternatives by calculating the (crisp) dominating areas in each pair consisted of triangular fuzzy sets (partial preorder); subsequently, the summation of the elements of each row (alternative) of the domination matrix gives a measure of the strength of each alternative that leads to the total preorder.

Table 3
Composition of the three NG-types to be transported through the Stefani-Aliveri pipeline.

Description	Units	Azerian gas	Russian gas	Algerian gas
Nitrogen	mol%	3.58	0.82	0.86
Methane	mol%	82.00	98.00	92.09
Ethane	mol%	7.60	0.70	6.23
Propane	mol%	2.55	0.21	0.71
i-Butane	mol%	–	–	0.05
n-Butane	mol%	1.60	0.08	0.06
Pentanes (C_5+)	mol%	0.64	0.07	–
Hydrogen Sulfide (H_2S)	mg/Nm^3	5.1	5.4	–
Mercaptan Sulfur	mg/Nm^3	15.3	16.1	–
Total Sulfur (inl. H_2S)	mg/Nm^3	70	107.3	–

3. Implementation

3.1. The implementation case

The methodology described above has been implemented in the case of potential leak detection of the Megara–Kalamaki branch extension designed for transporting gas to the Corinth industrial area (Fig. 3) [65]. The system, still in the early engineering phase, will, in general, have a design pressure of 70 barg, reduced to 40 barg where the pipelines pass through the urban areas of Athens, and will carry NG from Russian (through Romania/Boulgaria), Azerian (through Turkey), and Algerian (as cryogenic liquefied NG); the relative compositions are provided in Table 3 (stage 1 of the methodological framework presented above). The tracers used in the Russian and Azerian gas are hydrogen sulfide and mercaptans, with total sulfur reaching 107.3 mg/Nm^3 and 70 mg/Nm^3, respectively, for max. 48 h (stage 1); methane has been also considered as detecting moiety.

The proposed Megara to Kalamaki route currently passes close to Megara, mostly through sparsely populated undulating agricultural and rural areas and near two archaeological sites (stage 3). A 20" branch extension from Aghii Theodori continues to the Motor Oil refinery located nearby, passing through an environmentally protected area. The map provided indicates a railway and new national road. A motorway also tracks along the pipeline route to the South, following the coast line.

Actually, the design of balanced, effective and affordable leak detection systems is a complex engineering task. An ideal NG monitoring system should be capable of detecting and identifying gas traces in real time, running unattended for long periods of time, requiring infrequent maintenance and being inexpensive to operate [17,26]. Also, detection strategies should be closely following release mechanisms [33]; two scenarios can be considered: a low-level for detecting systematic leakage (i.e., slow release of low NG concentrations) and a high-level for detecting accidental leakage (i.e., immediate release of high NG concentration).

Thus, the detector at place should be able to operate at both, traces and high concentrations. Response times are crucial for triggering the counter mechanisms, along with the trade-offs among undetectability (missed alarms) and false alarms, linked to sensitivities, detection limits and number of sensors within the distributed network. Cost and reliability of the devices determine the number of detectors that can be installed [45]: the cheaper the detectors and the higher the reliability, the greater the number of devices to be spread along the pipeline. Reliability requires the minimization of undetectability and false alarm probability due to random factors on sensor readings. High sensitivity devices are desirable for early warning, especially when on-site confirmation is required for initiating the counter-measures [42]; thus, some redundancy is commonly allowed in sensors for ensuring adequate readings. More commonly, sensor faults occur because of the choice of the threshold [66]. Often, these are no real sensor faults but deviations due to measurement noise, which is inevitable. If the threshold setting is strict in order to suppress the missed alarm probability, the reading will be sensitive to random noise and temporary deviations, resulting in a high probability of false alarm. If the threshold is relaxed, accepting larger region to be considered as normal, then the number of false alarms will decrease with more missed alarms. Therefore, the reliability optimization problem of false alarms is a complementary criterion to the optimization problem of undetectability. In the trade-off between false alarms and missed alarms, missed alarms are often considered to be more important, supporting the adoption of sensitive redundant networks; adjacent detectors could provide overlapping coverage that, through a rules-based decision-support framework, will assist in ascertaining false alarms and other single-detector malfunctions. Notwithstanding, the severity of the counter mechanism initiated when the detector alarms should not be overlooked. Clearly, a detection system with a high false alarm rate cannot be employed to initiate a counter mechanism that involves long-term or irreversible impacts on operations, such as pipeline shutdown. However, a relatively high false alarm rate detector might be used to trigger a mechanism with mild or easily reversible impacts on operations, if a timely path is available to confirm the leakage. This fundamental design principle can be exploited to match the performance of a detection system to the unique characteristics of the pipeline under surveillance.

3.2. The formation of the set of alternatives

Although many gas detection systems have been reported in literature, only a few have been marketed and are operating, most developed on a semiconductor or a fiber-optic platform. A number of very promising prototypes have been recently hatched, such as the biosniffer of methyl mercaptan [52], offering continuous gas sampling and in-line sample preparation fluidics. The KB currently constructed by the authors contains 338 entries; each biosensor included has been decomposed to functional parts, which also takes into account the sampler and pre-concentration units, following the case organization hierarchy shown in Fig. 4. The general (upper) domains of the functional hierarchy include the target analyte, the detection strategy, the molecular recognition system, the transduction system, and the evaluation system. The detection strategy is defined to include: (i) the chemistry-based identification (CHE-ID) systems, relying on the identification of the chemical composition of the target molecules; (ii) the function-based identification (FCT-ID) systems, utilizing biological organisms or portions of organisms (tissue, cell, receptor, etc.) that react in a measurable way when exposed to a range of chemicals; (iii) the structured-based identification (STR-ID) systems, which include the affinity-based sensors, and (iv) the nucleic acid sequence-based identification (NAS-ID) systems, based on DNA or RNA sequence detection. The transduction systems usually employed for field devices are mainly of the amperometric type, although many optical devices are often employed in academic research. A plethora of biological systems has been used, including both natural and semi-synthetic materials.

The lower taxonomic levels are linked to the task (operational) hierarchy (Fig. 4), which contains structured information on sample, analysis, and recognition tasks. For example, a CHE-ID system *with* sequence_amplification *utilizes a* gas_sensing_array *involving the use of* tin_oxide_semiconductors and a gas_pattern_recogniser *based on* neuro-fuzzy network. Each instance (i.e., biosensor system) that is stored in the KB, is thus fully analyzed and described in any knowledge depth required by the user.

3.3. Fuzzy multicriteria selection of sensors

The set of sensors for methane, hydrogen sulfide, and mercaptans, as retrieved by the KB, include amperometric and optical devices (stage 7). The available methane detection methodologies [40,67–119] that obey the device specification criteria mentioned previously, are presented in Table 4. A pre-selection stage reduced the alternatives to nine, namely: continuous-wave cavity ring-down (CW-CRD) sensor [69], A1; the near infrared optical probe (NIR-S) [67], A2; the continuous auto gas chromatography (GC) system [72], A3; the tunable diode laser spectroscopy (TDLS) unit [75], A4; the photoacoustic laser spectrometer (PLS) [79], A5; the photoacoustic (PA) sensor [82], A6; the InGaAsP distributed feedback diode laser detector (NIR) [86], A7; the continuous wave, external cavity tunable diode laser (CRD) system [97], A8; the bacterial sensor (microscale) [99], A9. An expert panel set grades to the cri-

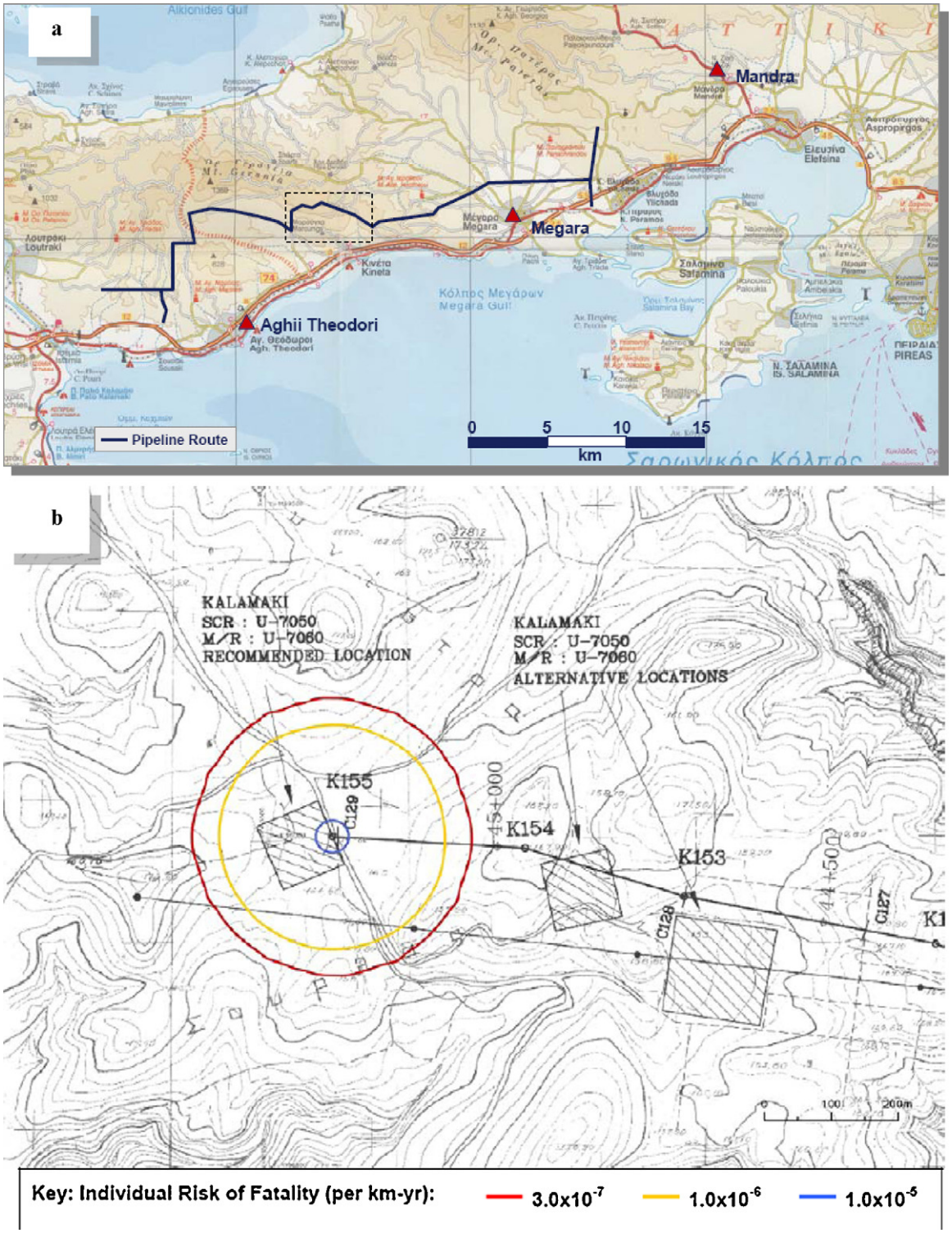

Fig. 3. The Megara–Corinth pipeline connection: the pipeline will terminate at Kalamaki but at a later stage the 30" pipeline will extend to Corinth industrial area and connect with the Northern Peloponnissos region. (a) Gas pipeline route to Corinth region; risk contours in typical scraper stations (per km-y): (b) Kalamaki station and (c) Megara west line valve station (source: ASPROFOS-Arthur D. Little [65]). The area contained within the dashed box in (a) has been used for the simulation presented in Fig. 8.

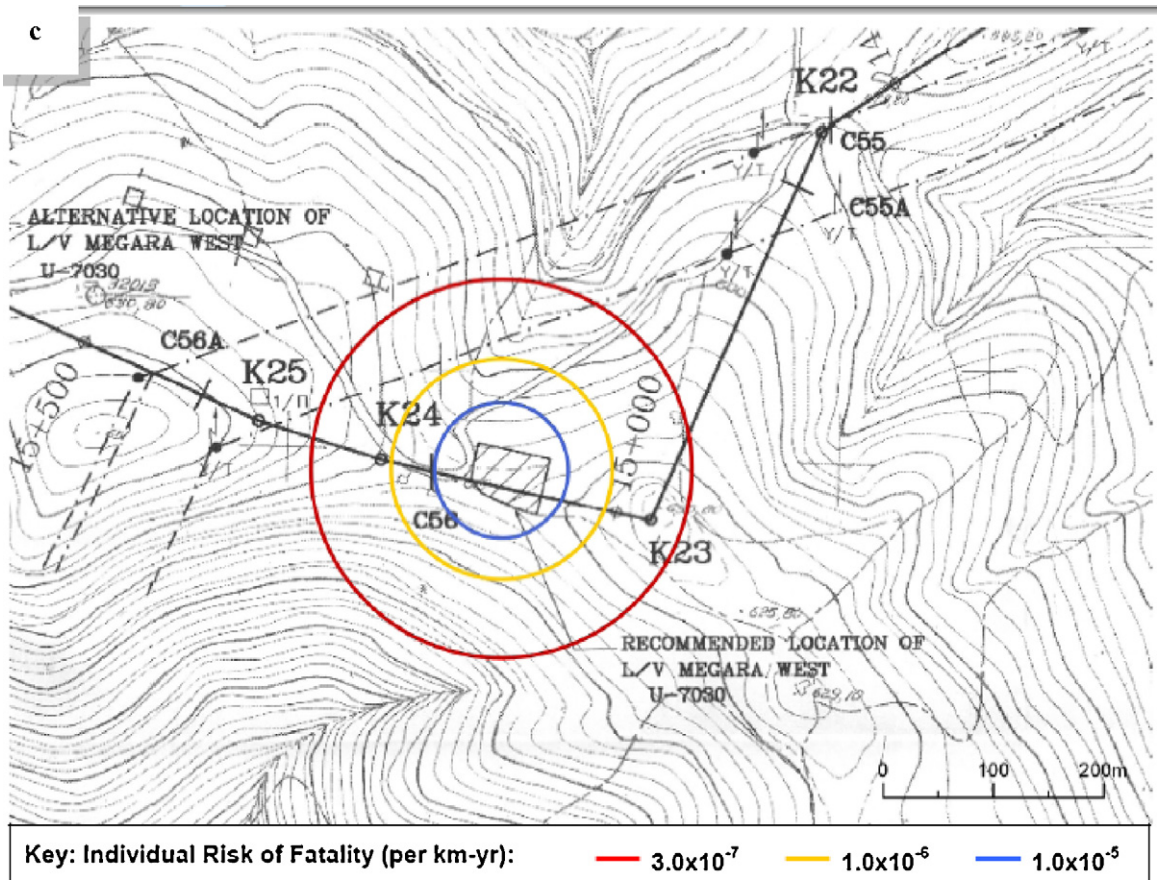

Fig. 3. (*Continued*).

teria vector and the preference matrix (stage 15) according to a properly modified Delphi method (as presented in [63]). The panel assembled to provide technical oversight on the proposed sensor designs, consisted of three academic researchers and two industry-related chemical engineers, representing sensor expertise currently engaged in biosensor technology. The biosensor network forms a thick network of innovation, i.e., a self-sustained system consisting of actors with endogenous knowledge and interest on this technology [49]; therefore, the assembly of a panel with specialists in sensors in the broad sense could not provide expertise (i.e., deep knowledge) for the technology at hand but most likely result in decreasing the objectivity of the selection process.

The results of stage 15 are shown in Fig. 5a, where partial ranking of alternatives (PRA) is shown as a set of circles with areas proportional to the crisp number *Sj*, which represents the corresponding relative value in the ranking vector. At low resolution ($q = 1.5$, $p = 3.0$) $S6 > S5 > S4 > S9 > S3 > S1 > S7 > S2 > S8$ implying A6 > A5 > A4 > A9 > A3 > A1 > A7 > A2 > A8; at high resolution ($q = 0.5$, $p = 1.0$) $S6 > S5 > S4 > S9 > S3 > S7 > S1 > S2 > S8$ implying A6 > A5 > A4 > A9 > A3 > A7 > A1 > A2 > A8, according to decreasing preference, as it is depicted in the diagrams of Fig. 5b, where the horizontal brackets stand for pairwise incomparabilities (also shown in the corresponding PRA diagram as alternatives in parallel setting). It is worthwhile noting that the order of triangle peaks (represented by the corresponding abscissa) of the triangular fuzzy numbers shown in Fig. 5a do not necessarily coincide with the multicriteria order, since defuzzification is based either on absolute area of each triangle (assumed to be concentrated at the centroid) or on pairwise comparison of areas (criterion Tseng and Klein [64], adopted herein); the higher the preference resolution level used the higher the probability of both (peaks and MCA results) orders to coincide, since the alternatives in the output fuzzy matrix or vector (PROMETHEE I or II, respectively) are more distinct.

In view of (i) the ranked first alternative A6, i.e., the photoacoustic (PA) sensor, is not involved with incomparabilities at both resolution levels, and (ii) monoparametric sensitivity analysis of A6 against the 'second best', i.e., the photoacoustic laser spectroscopy (PLS), within the range ±50% round the mean defuzzified value of each criterion (sensitivity analysis of each criterion, SAC) indicates that S6–S5 > 0, as shown in all SAC diagrams, we may conclude that the solution found is robust. Empirical evidence provided by experts and technical literature support the validity of the proposal as regards the ranked first alternative. Alternatives A1 and A8 are based on the cavity ring down technique that enables extremely high sensitivities because path length of kms can be realized provided highly reflective mirrors with reflectivities of >99.995% are employed [69,97]; obviously, such mirrors with multilayer dielectric coatings can only be produced for a limited wavelength range each [120]. Furthermore, a detector with high responsivity is needed which requires cryogenic cooling at IR wavelengths [69,97], raising substantially cost of production of field devices (criterion f_1) [120]. The NIR-based sensor [67], i.e., alternative A2, presents some reliability issues (criterion f_6) related to humidity effects: when moisture varies from sample to sample, as commonly seen with field samples, the varying interactions between water and other components cause poorer calibrations [121]. Alternative A7 uses one of the absorption lines for methane and is free from interference of absorption lines of water [86]; however, its noise level is relatively high, masking low concentrations of methane (criterion f_8). Notwithstanding, one caveat to the use of NIR-based technology is that although it is well suited to field portability and remote sensing, development and maintenance costs

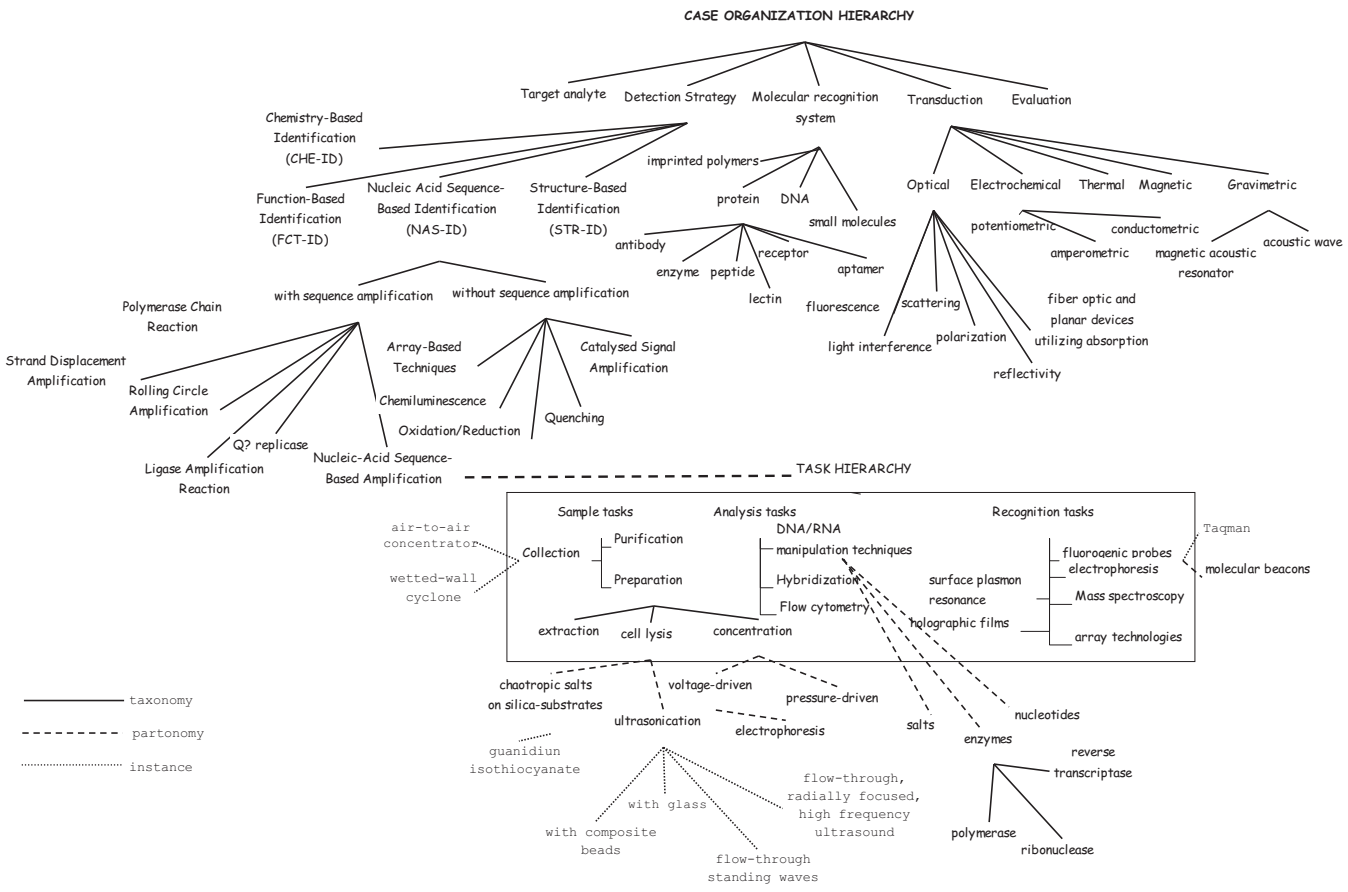

Fig. 4. The case organization hierarchy for hydrocarbon biosensor systems.

(especially calibration) are quite high [121]. Alternatives A3 (GC system) and A9 (microscale sensor) do not provide the required sensitivity (criterion f_3) and response time (criterion f_7), at reasonable cost [72,99]. The tunable diode laser spectroscopy system (alternative A4) offers substantial benefits on production scale that, in the near future, are expected to generate a lowered energy consumption device and less maintenance of equipment [75]. The cost of these systems, however, is still relatively high and their application is usually limited to situations where an integrated measurement of methane gas density over relatively long open path lengths is required [122]; consequently, the system is typically used to measure the presence of clouds of gas within lengths of the order of meters. According to the experts opinion, photoacoustic technology (alternatives A5 and A6) offers a realistic potential to the development of field sensors based on compactness of the systems, the ease of use, their ability to operate at atmospheric pressure and their insensitivity to optical misalignment. Although PLS is more attractive and has a very weak volume of cell that gives the possibility to develop a high-speed moving monitor [79], its high development costs ranked it second; the lower-cost and simpler PA sensor shows better techno-economic feasibility for long-term and large scale pipeline surveillance.

Field determinations of mercaptans in natural gas (stage 15) are important because of the tendency of the mercaptan concentration to fade over time. The current procedure for testing mercaptan vapors *in situ* uses the length-of-stain detector tubes, conforming to ASTM D1988-06 for total mercaptans [123] or ASTM D5305-97 for ethyl mercaptan [124]. Standard methodology is inappropriate for continuous field monitoring as it relies on a colorimetric semi-quantitative assessment followed by laboratory chromatography for accurate quantitative determination. Up to the present, many techniques have been attempted for the determination of thiol vapors. State-of-the-art detection methods with both specificity and sensitivity for sulfurous molecules, as retrieved by the KB (stage 22) and external bases (stage 23), often require bulky, sophisticated instrumentation such as gas chromatography with flame photometric detector. Gas chromatography with a sulfur chemiluminescence detector has high selectivity and a wide line arrange [125], in which the sulfur-containing substances can be converted into SO_2 in a hydrogen/oxygen furnace and subsequent ozone-induced chemiluminescence; gas chromatography with atomic emission detection [126] or mass spectrum has also been reported [127], but it has been rejected as an option based on its high cost and highly skilled analysts required. Some of these techniques may additionally require preconcentration of the vapor prior to detection. Other field gas sensing systems with the required sensitivity, selectivity and response time include (i) a sorption-based detector approach utilizes films of Au nanocrystals capped with organic ligands [128], and (ii) the biosniffer [52], a Clark-type dissolved oxygen electrode with a monoamine oxidase immobilized membrane. While the former is relatively costly as per manufacturing and maintenance, the latter is simpler in assembly and has been field tested successfully. Therefore, the best option for mercaptan detection is given by the biosniffer [52]; in order to amplify the biosensor output, a substrate regeneration cycle caused by coupling the monooxygenase with L-ascorbic acid as reducing reagent system is applied. The biosniffer is calibrated against methyl mercaptan vapor from 0.01 to 10 ppm and gives a detection limit of 0.2 ppm (the human sense of smell level 5).

As regards hydrogen sulfide detection, instrumental techniques dominate the literature with the increased sensitivity largely displacing the more classical approaches. The various routes that have

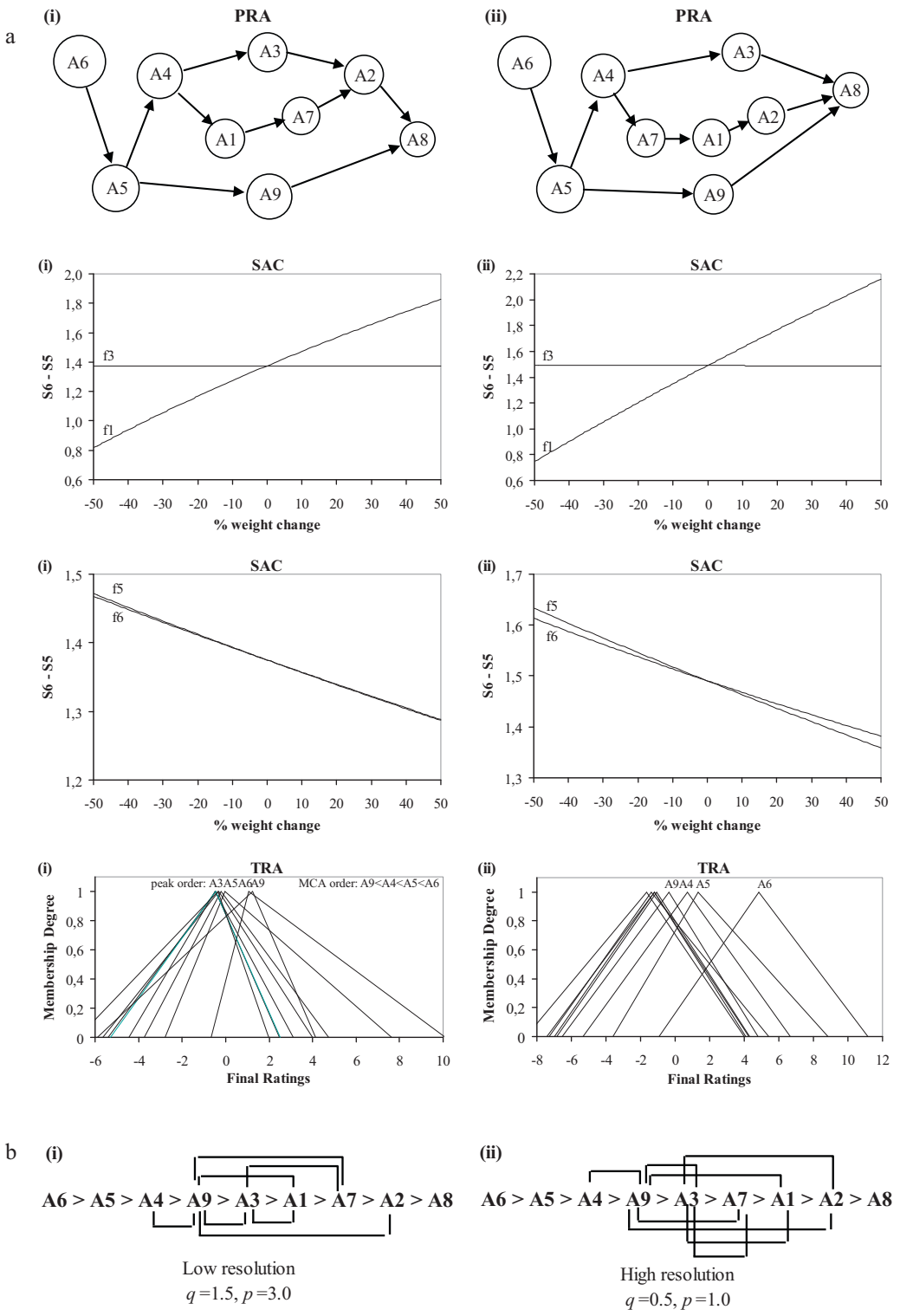

Fig. 5. (a) Partial ranking of alternatives (PRA), sensitivity analysis of each criterion (SAC), and total ranking of alternatives (TRA), in triangular fuzzy form, at (i) low preferability resolution with medium q, p values and (ii) high preferability resolution with low q, p values; the arrow '→' means '*better than*'. The nine alternatives considered for methane detection within a NG pipeline leak detection network are: continuous-wave cavity ring-down (CW-CRD) sensor, A1; near infrared optical probe (NIR-S), A2; continuous auto gas chromatography (GC) system, A3; tunable diode laser spectroscopy (TDLS) unit, A4; photoacoustic laser spectrometer (PLS), A5; photoacoustic (PA) sensor, A6; InGaAsP distributed feedback diode laser detector (NIR), A7; continuous wave, external cavity tunable diode laser (CRD) system, A8; bacterial sensor (microscale), A9. At both resolution levels, alternative A6 (the PA sensor) prevails, while the SAC graphs indicate that this is a robust solution, since the difference (S6–S5), S5 quantifying the second-best alternative A5, i.e., the PLS sensor, is positive over the whole range ±50% of the weight change examined for each criterion. (b) Diagrams depicting the decreasing preference of the alternatives; horizontal brackets stand for pairwise incomparabilities.

Table 4
Analytical characteristics of methane detection methodologies.

Technique	Sample	Detection range	Detection limit	Nomenclature used in MCA	Refs.
NIR S	Water	n/s	1 μM	A2	[67]
MID IR	Air	n/s	100 ppm		[68]
CW-CRD	Air	n/s	2 ppm	A1	[69]
GC-PDHI	Air	100–1000 nL/L	100 nL/L		[70]
PA	Air	n/s	120 ppm		[71]
GC	Air	n/s	2 ppm	A3	[72]
MPA	Soil	50–10,000 μL/L	50 μL/L		[73]
CS	Air	0.1–1%	0.10%		[74]
TDLS	Air	n/s	1 ppb	A4	[75]
FT-IR	Water	1.5–2.5 ppm	1.5 ppm		[76]
MID IR	Air	n/s	ppt		[77]
PL	Water	1–10 ppm	1 ppm		[78]
PLS	Air	n/s	3 ppb	A5	[79]
TDLS	Air	20–200 ppm	20 ppm		[80]
BS	Air	10–500 ppm	10 ppm		[81]
PA	Air	n/s	0.2 ppb	A6	[82]
BS	Air	100–1000 ppm	100 ppm		[83]
MID IR	Air	n/s	2%		[84]
PA	Air	n/s	0.2 ppb		[85]
NIR	Land fills	n/s	5 ppm	A7	[86]
PA	Air	n/s	20 ppm		[87]
EL	Air	6–100 ppm	6 ppm		[88]
GC-PDHI	Human breath	0.3–400 ppmv	0.3 ppm		[89]
Calorimetric	Air	0–2.5%	>0.125%		[90]
GC-FI	Air	1 ppm–100%	1 ppm		[91]
GC-FI	Air	n/s	35 ppb		[92]
GV-FI	Air	n/s	0.15 μg/L		[93]
MID IR	Air	n/s	2 ppb		[94]
NIR	Air	n/s	20 ppbv		[95]
CRD	Air	n/s	52 ppbv		[96]
CRD	Air	n/s	4 ppb	A8	[97]
MID IR	Air	n/s	105 ppt		[98]
Microscale	Aqueous	n/s	0.14 μmol	A9	[99]
Solid state	Anaerobic	1–20%	n/s		[100]
Calorimetric	Air	0.25–300 ppmv	0.25 ppmv		[101]
NIR	Air	n/s	30 ppb		[102]
Solid state	Air	>4150 ppm	n/s		[103]
Solid state	Air	n/s	100 ppm		[104]
Solid state	Air	0.02–5.5%	0.02%		[105]
Solid state	Water	n/s	0.55 ppm		[106]
Solid state	Air	0–500 ppm	n/s		[107]
MID IR	Air	n/s	170 ppm		[108]
NIR	Air	n/s	2.5 ppm		[109]
Microscale	Rice paddy	n/s	1 μM		[110]
Solid state	Air	n/s	2000 ppm		[111]
Solid state	Air	n/s	500 ppm		[112]
GC-PA	Air	n/s	1 ppbv		[113]
Microscale	Aqueous	0–1 atm	μM		[114]
Calorimetric	Air	n/s	0.50%		[40]
NIR	Air	0.2–100%	0.20%		[115]
Solid state	Air	n/s	0.10%		[116]
Solid state	Air	0.01–5.5%	0.01%		[117]
Piezoelectric	Air	n/s	0.018 vol%		[118]
Calorimetric	Air	n/s	1%		[119]

BS, biosensor; CRD, cavity ring-down spectroscopy; CS, chemical sensor; CW, continuous wave excitation; FI, flame ionization; FT-IR, Fourier transform infrared spectroscopy; GC, gas chromatography; MID IR, mid infrared spectroscopy; MIS, metal–insulator–semiconductor; MPA, membrane flushing probe array; NIR, near infrared; PA, photoacoustic sensor; PDHI, pulsed discharge helium ionization; PFPD, pulsed flame photometric detection; PL, photoluminescence; PLS, photoacoustic laser spectroscopy; S, sensor; TDLS, tunable diode laser spectroscopy; n/s, none specified.

been considered in the analysis of sulfide are broadly summarized in Fig. 6; spectroscopic procedures [129–141] are undoubtedly the most common routes taken, along with chromatographic [142–151] and electrochemical [152–158] techniques. The KB (stage 22) also produced alternative detection methods [159–177], such as elemental analysis [159], electronic noses [160], luminescent sorbent tubes [161], colorimetric [162,163], biosensors and chemical sensors [164–166], and solid state systems [167–174]. The analytical characteristics of the techniques mentioned have been summarized in Table 5 for ease of comparison. Despite significant advances in instrumentation, most of the detection systems shown in Fig. 6 and listed in Table 5 are, however, still reliant upon some form of sample manipulation for the required selectivity, that adds considerably to cost. Furthermore, the detection of gas samples is quite problematic, especially at low concentrations [153,155,178]: the evolved gas is extremely reactive and will readily adsorb onto surfaces; while this is a feature that is actively exploited in a number of analytical protocols [132,140,155–158,167,171–176], it can be the source of erroneous results and poor recoveries, particularly when dealing with field assessments [178–180]. Elimination of such problems is a non-trivial task and requires careful handling by trained personnel and the utilization of 'deactivated' surfaces where appropriate. Sensor calibration, especially *in situ*, may cause additional problems; the preparation of calibration stan-

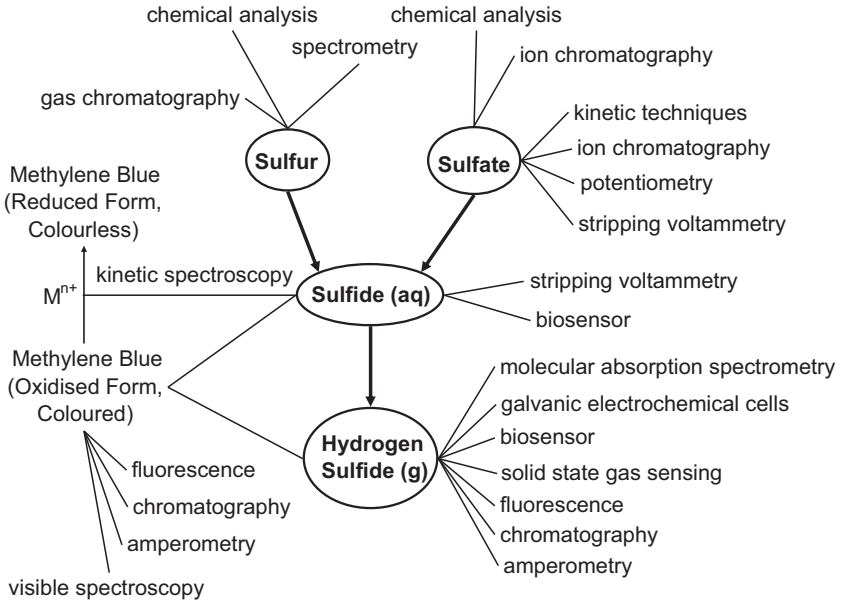

Fig. 6. Analytical pathways for the detection of sulfides.

dards requires a considerable degree of care, caution and indeed scrutiny of all aspects of the experimental equipment [178–180]. This is particularly important when preparing low concentrations of the analyte, whereby losses through aerial oxidation or reaction with trace metal impurities (particularly copper [153,155]) can be significant. Notwithstanding, each sensor category bears along its own limitations that prohibit presently the development of field devices: spectroscopy cannot be used for direct quantitation as successful implementation of this approach still requires a degree of sample preparation [129–140]; the selectivity of electrochemical sensors remains an issue with other thiols (as mercaptans that are expected in the sample) and reducing agents [152–158]; chromatography requires column separation to compensate for the lack of selectivity with respect to other redox species [142–147]; solid state systems are generally susceptible to temperature and humidity fluctuations and typically offer less selectivity that other technologies [167–174].

In view of the above and considering the intended task of pipeline stand-alone surveillance, none of the available sensors can fit the required specifications. The decomposition–recomposition procedure (stages 9–10) provided four alternative designs. The best option (stage 11), determined on the basis of the h-set of criteria pertinent to experimental set-ups (see Section 2), is presented by a novel biosensor (Fig. 7), which utilizes (a) a pre-treatment unit that converts gas hydrogen sulfide to sulfate ions in an aqueous solution [181], (b) a microbial cascade unit for converting sulfates to sulfides, adapted from [182], and (c) the horseradish peroxidase biosensor of Liu et al. [164] (the 8th system in Table 5), which detects the inflow sulfides from the degree of their inhibition to the enzyme activity. This biosensor option, although still untested as complete set-up, has been rendered feasible at reasonable development costs, especially as per h_2, h_3 and h_7 criteria, as (i) it depends on a simple assembly that can be developed applying continuous innovative action, (ii) the system is presumably interference-free and can handle the reactivity of the analyte, and (iii) the sensitivity and selectivity are expected to be more than adequate for the expected concentrations. The solution is robust, provided, of course, that the results from testing (stage 12) are satisfactory and that the device is locally developed and produced.

3.4. Validation issues

A small-scale, simplified, simulation has been performed, just for illustrating the behavior of the implementation scheme proposed, in a 12.5 km pipeline section that passes through the medium-density populated region of Kineta, around 15 km east of the city Corinth and about 60 km west of Athens. The design of the sensor network, including the three sensors selected for methane, mercaptans and hydrogen sulfide, was based on a modification of the Trachtam algorithm [183], initially developed for water monitoring on an engineering strawman approach, taking into consideration factors such as population distribution, system pressure and flow patterns, critical customer locations, sensor reliable measurement radius, wind direction and speed, dilution rates and convection currents. Eleven nodes have been proposed and tested with two scenarios (Fig. 8): scenario 1 involves a 22 sensors solution in which a methane sensor is placed in each node, whereas the 6 nodes near residential areas are also packed with mercaptan sensors and 5 nodes with sulfide sensors; scenario 2 gives a 9 sensors solution with 4 methane detectors, 2 mercaptan detectors and 3 hydrogen sulfide detectors.

The network has been evaluated using only two quantitative design objectives, i.e., the expected time of detection and the detection likelihood. For a particular NG constituent leakage scenario, the expected time of detection by a sensor, Z_1, is the elapsed time from the start of the leak event, to the first identified presence of a non-zero (i.e., above background) NG constituent concentration. The time of first detection, t_j, refers to the jth sensor location. The critical time of detection for the sensor network for a particular leakage event, t_d, is the minimum among all sensors present in the design, i.e., $t_d = \min t_j$. The objective function to be minimized is the expected value computed over the assumed probability distribution of leakage events, i.e., $Z_1 = E(t_d)$, where $E(t_d)$ denotes the mathematical expectation of the minimum detection time t_d. Since missed alarms have no detection times, they were not included in the analysis. Given a sensor network design (i.e., number and locations) the detection likelihood, Z_4 (i.e., the probability of detection), is estimated by $Z_4 = (1/S)\sum_{r=1}^{S} d_r$ where $d_r = 1$ if the NG constituent r is detected, and zero otherwise; S denotes the total number of NG constituents considered. Z_4 is to be maximized.

Table 5
Analytical characteristics of hydrogen sulfide detection methodologies.

Technique	Sample	Detection range	Detection limit	Refs.
EL	Aqueous	40–660 nmol/L	40 nmol/L	[152]
Solid state	Gas	10–250 ppm	10 ppm	[167]
Colorimetric	Gas	50 ppb–5 ppm	50 ppb	[162]
MIS	Gas	200 ppb–10 ppm	200 ppb	[168]
MIS	Gas	n/s	1 ppm	[169]
GC-PFPD	Gas	2.08–208 ppmv	2.08 ppmv	[142]
ICPA-ES	Aqueous	5–25 μg/L	5 μg/L	[129]
BS	Water	0.1–38.5 μmol/L	0.05 μmol/L	[164]
MIS	Gas	n/s	25 ppm	[170]
Colorimetric	Gas	10–100 ppm	10 ppm	[163]
GC-PFPD	Wine	0.36 ppbv–1.5 ppbv	0.36 ppbv	[143]
ESD	Gas	n/s	12 ppm	[175]
Solid state	Air	200–3000 ppb	200 ppb	[171]
CS	Gas	0.010–0.054%	0.010%	[165]
GC	Gas	0.36 ppmv–1.5 ppmv	0.36 ppmv	[144]
EL	Aqueous	0.02–1 mM	14 μM	[153]
LC-AFS	Aqueous	n/s	9.7 μg/L	[130]
EL	Aqueous	0.04–700 μM	0.04 μM	[154]
CS	Aqueous	4.6 μg/L–100 mg/L	50 μg/L	[166]
Solid state	Gas	n/s	0.1 ppm	[172]
GC-PFPD	Gas	10–100 ppmv	10 ppm	[145]
Solid state	Gas	n/s	250 ppbv	[173]
Solid state	Gas	n/s	1 ppb	[174]
DPP	Petroleum	n/s	410 ng/g	[176]
GC-PFPD	Gas effluents	n/s	5 μg/m^3	[146]
EL	Aqueous	20–200μM	20 μM	[155]
EL	Aqueous	n/s	0.1 ppm	[156]
Fluorescence	Human breath	4–200 ppb/v	4 ppb/v	[131]
GC	Aqueous effluents	490–4900 ppb	0.49 ppb	[147]
ION GC	n/s	35–50 ppm	35 ppm	[148]
CE	Mining water	0.05–15 ppm	0.05 ppm	[177]
ELEM ANAL	Sediment	0.02–2.84%	0.034%	[159]
Electronic nose	Landfill	125–781,066 odor units/m^3	n/s	[160]
Fluorescence	Aqueous	2.24–141 ppb	2.5 ppb	[132]
LUMIN SORBENT TUBES	Air	0.2–1.3 ppm	n/s	[161]
EL	Aqueous	n/s	2 ppm	[157]
ION GC	Dairy farm effluent	3–50 ppm	3.7 ppm	[149]
ION GC	Hot spring water	0–16 ppb	0.14 ppb	[150]
LC	Seawater	12–25.6 ppm	12.8 ppm	[151]
Fluorescence	Air	10–100 ppb/v	10 ppb/v	[133]
Mol. absorption	Waste streams	0–100 ppm	0.13 ppm	[134]
EL	Aqueous	0.2–200 ppb	0.9 ppb	[158]
Fluorescence	Aqueous	1.792–640 ppb	n/s	[135]
Fluorescence	Aqueous	0.08–15 ppm	80 ppb	[136]
Kinetic-UV/vis	Spring water	50–2000 ppb	n/s	[137]
Kinetic-UV/vis	Spring water	0.01–25 ppb	0.015 ppb	[138]
Kinetic-UV/vis	Spring water	50–6000 ppb	n/s	[139]
Mol. absorption	Mineral water	50–700 ppm	50 ppm	[140]
Kinetic-UV/vis	Blood	0.016–16 ppm	32 ppb	[141]

AFS, atomic fluorescence spectrometry; BS, biosensor; CE, capillary electrophoresis; CS, chemical sensor; DPP, differential pulse polarography; EL, electrochemical; ELEM ANAL, elemental analyzer; ESD, electrostatic spray; GC, gas chromatography; ICPA-ES, inductively coupled plasma-atomic emission spectroscopy; ION GC, ion chromatography; LC, liquid chromatography; LUMIN SORBENT TUBES, luminescent sorbent tubes; MIS, metal–insulator–semiconductor; n/s, none specified.

Sensor response times for methane and mercaptan sensors were taken at reported value, i.e., 100 s [82] and 60 s [52], respectively. The response time for the hydrogen sulfide sensor unit was roughly estimated to 110 s, allowing for adequate reaction time and signal transmission from one functional part to the next (Fig. 7).

Three leakage events have been simulated, namely A, B, and C, at points randomly selected, at very low to low concentrations for all analytes and at a wind speed of 7 m/s (4 Beuafort). Events A and B implicated one leakage point, whereas at event C two locations were involved with leaks beginning at the same time. In all cases, scenario 1 gives a detection likelihood of above 0.7, whereas the 9 sensors solution seems appropriate only for confirmation of leakage events reported by the conventional survey system. The expected time of detection for scenario 1 was ca. 380 s for events A and B, but it reduced to ca. 280 s when two leaks occurred at different locations at the same time (event C). Diffusion patterns and cloud formation should also be carefully considered for a realistic network design, in which case geomorphology and prevailing meteorological conditions (extracted from spatio-temporal data distribution) are of significant importance.

Evidently, the network requires extensive validation (stages 12–17 of the methodological framework), both under simulated and real operation conditions, in order to prove its suitability for the intended task. At stage 12, the developed/adopted/modified sensors are evaluated on a laboratory testing bench under a large range of analyte concentrations, interferences, flow rates, temperatures and humidity, with special attention to the determination of sensitivity and selectivity of detection, as well as response times and reliability of measurements, in terms of reproducibility, accuracy and reversibility of the signals in such conditions. The results gathered would provide for a fault detection expert system, structured in accordance with the format developed in [47,48], and appropriate remedial activities (on-line, in-line and off-line) should be tested and ranked as per cost, efficiency, and easiness of application.

An important issue that should be addressed at this phase is the bioelement-dependent operational life time, in terms of the

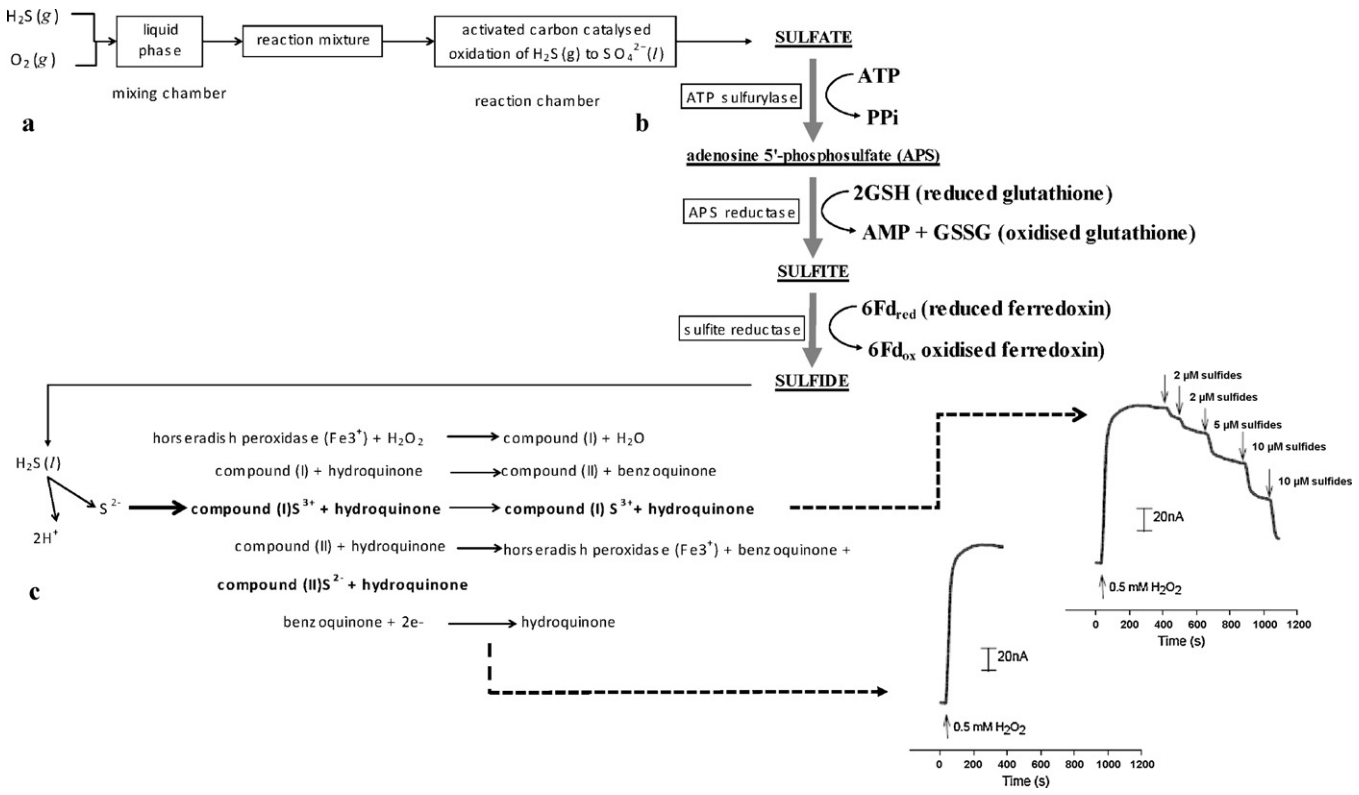

Fig. 7. The recomposed biosensor for hydrogen sulfide, provided after the activation of stages 9 and 10 of the algorithmic procedure. The main functional part consists of an inhibition sulfide biosensor constructed by layer-by-layer technique based on horseradish peroxidase (c); the biosensor detects hydrogen sulfide at aqueous samples. The transformation of gas sulfide to sulfide ions is achieved through (a) the gas-to-liquid converter that produces sulfate ions in aqueous solution, and (b) the microbial conversion of sulfate to sulfites which actually are fed into (c).

stress level (i.e., extreme conditions, interferences, high concentrations) that the sensor is expected to endure under real working conditions [61]. Although biosensors are costume-designed to accommodate the shelf life and stability of the labile biomaterial [47,48], relevant scientific or technical literature is scarce [184,185]. Ageing is often one of the deciding factors in configuring the maintenance/replacement protocol: the immobilized moieties (e.g., proteinaceous molecules) are subject to activity loss due to denaturation and/or deactivation, thus diminishing the life of the sensor [47,48]. In some previous work, the authors reported a replacement/maintenance program for a similar surveillance network in landfills [185]. The program, adopted to suit the needs of the present work, is based on (a) the Weibull Distribution (WD), which is widely accepted in reliability problems and life data analysis due to its versatility and (b) an Arrhenius type equation, relating the WD scale parameter or biosensor characteristic life η to stress level V according to the expression $\eta = A\exp(B/V)$, where the independent variable V takes values from the data set $[I_j, V_j]$; the index I_j is the crisp output of a fuzzy rule that evaluates the effect of temperature/humidity – mean values and their fluctuations (in order to take fatigue due to environmental changes under consideration). By substituting for η in the WD probability density function (pdf), the following expression is obtained, which is the backbone for the biosensors replacement program:

$$f(T,V) = \frac{\beta}{A\exp(B/V)}\left(\frac{T}{A\exp(B/V)}\right)^{\beta-1}\exp\left[-\left(\frac{T}{A\exp(B/V)}\right)^{\beta}\right]$$

where T is the operational life time of the biosensor, as determined by the level of stress it endures [61], β is the Weibull shape parameter and A, B the Arrhenius equation parameters. For this pdf, the reliabilities function $R(T,V)$ the failure rate function $\lambda(T, V)$, and the reliable life T_R of a biosensor for specified reliability (starting its operation at age zero), are estimated by means of the following expressions:

$$R(T,V) = \exp\left[-\left(\frac{T}{A\exp(B/V)}\right)^{\beta}\right]$$

$$\lambda(T,V) = \frac{f(T,V)}{R(T,V)} = \frac{\beta}{A\exp(B/V)}\left(\frac{T}{A\exp(B/V)}\right)^{\beta-1}$$

$$T_R = A\exp(B/V)[-\ln(R(T_R,V))]^{1/\beta}$$

The latter expression gives the life for which a biosensor is expected to operate successfully with a reliability level of $R(T_R)$. In the special case that $R(T_R) = 1/2$, the T_R-value gives the half (or estimated median) life, i.e., the life time by which half of the biosensors installed in each pipeline section remain still fully operational.

Functional verification (stage 16) moves to the field for signal validation, aiming at establishing a relationship between the measure and key parameters affecting signal generation and transmission. At this phase, an initial pipeline route section is monitored by both, sensors and conventional equipment, allowing for adequate redundancy in order to provide reliable estimates of failure rates. The signal measurements (sensor outputs) are compared with their estimates reconstructed by outputs of other similar sensors and checked against the conventional surveillance network responses and, if necessary and applicable, lab analysis; the difference between signal measurements and estimations, i.e., the residual signals, are then analyzed by either deterministic or stochastic rules to determine if the observed signal sequence has fault. A variety of methods have been developed for system modeling and signal reconstruction, including artificial neural networks

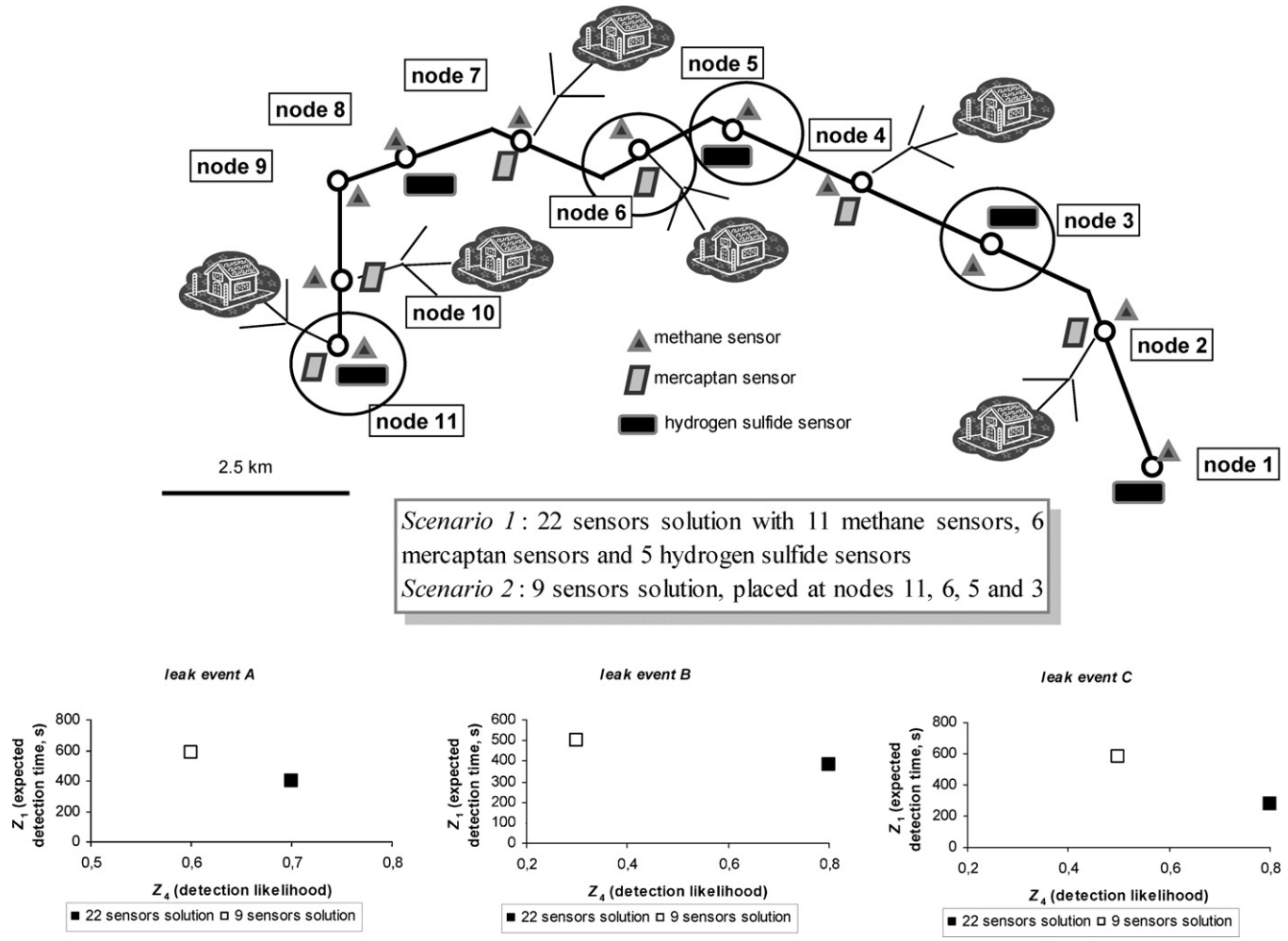

Fig. 8. Small-scale simulation for illustrating the behavior of the implementation scheme proposed, in a 12.5 km pipeline section that passes through Kineta region. The solutions layout for eleven nodes (upper scheme) involves two case scenarios: a 22-sensors network and a 9-sensors network (circled nodes). Three leakage events have been simulated, namely A, B, and C, at points randomly selected; events A and B implicated one leakage point, whereas at event C two locations were involved with leaks beginning at the same time. The expected time of detection, Z_1, versus the detection likelihood, Z_4, for each event and scenario are shown in the bottom. In all cases, the 22-sensors layout gives a detection likelihood of above 0.7, whereas the 9-sensors layout seems appropriate only for confirmation of leakage events reported by the conventional survey system.

(ANN) based methods [186], principle component analysis [187] or its derivative independent component analysis [188], multivariate state estimation technique [189], and support vector machines [190].

Pilot testing in the field follows a circular pattern, where the hybrid network established in a pipeline section moves to the next section, and so on, until all the final adjustments/refinements/corrections are made and the monitoring scheme is rendered reliable for a long-term application. Thereafter, the network may shift mostly to biosensing, requiring, however, periodic controls with conventional instrumentation, according to the system of survey and certification that will be adopted. Thus, biosensors' lack for standardization procedures/practices is successfully overcome, since the incurred routine inspection adds considerably to the reliability of the pipeline leak monitoring scheme. The frequency/intensity of these inspections can be modified according to the evaluation of the signal retrieved by the sensors; for example, an alarming situation revealed by field signals (e.g., increasing trend of methane concentration) would prompt an *in situ* investigation/verification with either the thickening of the biosensor network (i.e., increasing the number of sensors or placing sensors of higher selectivity/sensitivity) in the alarming area or with conventional detectors.

This validation approach has been utilized successfully by the authors to a number of environmental systems, including underground mine fields [184], landfills [185], oil refineries [191], forestrated areas [45,192] and wetlands [46]. These projects addressed multi-elemental monitoring in both phases, the gas and the liquid, through a regional network around a pollution source in the form of a local area network (LAN), with on-line data collection and mining, as regards biosensoring. Undoubtedly, the implementation of the proposed scheme is by far more feasible in both, technical and economic terms, when the pipeline network is still in the early engineering design phase. In most cases, the construction of the network and the installation of the surveillance system take effect concurrently. The costs for replacing the monitoring system or for adding sensor elements in an operating pipeline is extremely high. Furthermore, the structure of the presented framework is such that facilitates the gradual field validation and operation as the pipeline is assembled segment-by-segment. Note, however, that at the present state any activity-based costing is impossible, even as a rough estimation, since it depends on many parameters, including the stage of technological development of the adopted sensor (i.e., ready-to use, experimental set-up or basic research level), know-how transfer models and local production feasibility at appropriate subsidization [49].

4. Discussion

Most of the conventional leak detection systems to date for natural gas pipeline networks, have in general failed to perform optimally within the restrictions of response time, robustness, reliability, sensitivity, accuracy and cost. Biosensing effectively addresses the issues of rapid response, sensitivity and accuracy, offering a suitable and cost-effective alternative to long-term, in-line pipeline network monitoring, provided that mass production and standardization of the related technology is feasible.

The methodological framework presented herein considers both evaluation and management tasks supporting timely NG leak detection surveillance; it permits on site validation and standardization of novel biosensors with the use of appropriate conventional detectors in a cost-effective manner (stage 16 of the methodological framework), since the main objective is the gradual withdrawal of the detectors and the shifting of the monitoring system mostly to biosensing (stage 17 of the methodological framework). The proposed methodology can assist both, the moving of biosensors from the lab to the field and the efficient large-scale surveillance of critical NG infrastructure, provided that a well-structured KB is established and maintained. The large number of features used to describe a biosensor, however, coupled with the wide range of values that many of these features can assume, makes it practically impossible to store every possible case detail in the system's KB. Biosensors carry a wide variety of specifications referring to manufacturing, testing, operational requirements, metrological characteristics, fault diagnostics, etc. It therefore becomes particularly important to select cases and features in a fashion that provides an adequate coverage of the range of problems the system is expected to face and, at the same time, keeps the size of the knowledge base manageable. The decomposition/recomposition module proposed herein offers the benefit of greatly reducing the amount of effort required in the knowledge engineering task. The drawback of applying this scheme, however, is that if raw low-level data is used, due to its representational sparseness, it is generally necessary to collect a greater population sample in order to construct a case base with adequate coverage [46]. Alternatively, human experts, as employed herein for running the multicriteria analysis selections, or even automated induction, clustering or other techniques can be used to construct a more restricted description space that carries the most critical to the decision-maker case information; certainly there exists a tradeoff in the extra effort required to construct these representations, an effort that should be repeated whenever it is desired to expand the role of the system.

Notwithstanding, the validation of field biosensors through conventional detectors *in situ* is inevitable and bears a substantial cost. Biosensors can be affected by a variety of parameters, which are not only dependent on the geographic area, but also on atmospheric conditions, which change along the day and the year. Measurements should be therefore correlated and evaluated on the basis of the applicable codes and standards for NG pipeline leakage survey, such as the ASME B31.8-2007 [193], employing surface and sub-surface gas detection (including bar hole surveys), pressure monitoring, and ultrasonic leakage tests, in combination with thermometers, hygrometers, etc. These additional costs would deeply reduce the cost-effectiveness of biosensors in the short-run. On the other hand, the merits of such a demand-driven approach do not only include the development of effective, prompt, direct and reliable means of leak detection over the mileage of pipeline network, but further extend to issues related to management of large-scale and long-term monitoring schemes as (i) it serves as a practical means for standardizing biosensors, given that no direct standardization protocol or guidelines exist (mainly due to the involvement of biological elements and their direct connection to transduction systems [49]), (ii) it adds trust to the reliability of the long-term monitoring scheme, and (iii) it can encourage the local production of ready-to-market/use devices, utilizing indigenous materials and taken advantage of scale economies due to large production. Furthermore, the experience obtained and the developed set of field biosensors and supporting equipment used for engaging and maintaining the monitoring scheme in one NG network can be used, mostly as is, in starting-up/maintaining a similar scheme for another pipeline network. It is worthwhile noting that in the time-course, the expected validation cost will decrease in the long-run as a result of (a) human experience accumulation and (b) incorporating know-how within the system itself. This is a common characteristic in systems approach to multi- and inter-disciplinary issues, as it has been stressed by several authors engaged with solving problems in different disciplines; e.g., Senge [194] and Bellamy et al. [195], argue about some kind of 'learning organization' that by means of a systemic view leads to knowledge enrichment, implying progressive improvement of the system itself.

Since the ultimate goal of pipeline surveillance is to detect leaks, ideally at the time they are created, i.e., shortly after the defect on the pipeline (rupture or hole) becomes critical [10,33,41], early detection and characterization of a nascent leak significantly increases the probability that a timely solution can be found. This admittedly involves the development of field biosensors with the appropriate sensitivity and selectivity, that, in such a case, depend at large upon the proper treatment of the matrix effects, i.e., effects associated with a unique local matrix which adversely impact the performance of an analytical process [196]; the impacts may include increased false positive or false negative rates, low or high bias or poorer precision. The identification/determination of this local matrix for tailoring biosensors can be only achieved when the segmentation of the surveyed area goes beyond the current precepts of statistical representativeness of grids that is linked only to the issues of number and distribution of sensors that should be placed to cover adequately the area to be monitored. Segmentation, as proposed herein, effectively relates to some kind of area classification into sections with similar characteristics in geomorphology, abiotic factors (light, temperature, humidity, soil composition, etc.), levels of background pollution (methane, NO_x, NH_4^+, SO_2, etc.), biotic factors (micro-flora and fauna, as these can alter drastically the local micro-environment), etc. Thereby, a series of similar (as per the target analyte) but differentiated (as per the operational environment) biosensors should be (i) developed and produced, following the special requirements of the various segments recognized in the area, and (ii) placed in the corresponding segment. The development of devices tailored to suit local background conditions may result in reducing substantially the false alarm rate per detector, since random noise and temporary deviations compensation is built-in by design, provided that the differentiated sensors are calibrated *in situ*. In effect, this approach may bring biosensors closer to the production of a stand-alone surveillance network with efficiencies that supersede conventional instrumentation and current patrol practices.

If surveillance calls for more information or higher information granularity, more biosensors should be placed in the field. In such a case, however, the cost is neither simply proportionally higher (as when purchasing a number of the same biosensors) to the initial estimations, nor decreasing (as it would be at mass production of the same biosensors due to scale economies), but disproportionally higher as it actually involves the tailoring design/development/production/implementation/maintenance of these differentiated biosensors (DBs), intended to cover a higher number of differentiated segments. Under this standpoint, the convexity of the cost curve is maintained, which is a necessary condition for the optimization method that is described subsequently in a conceptual way.

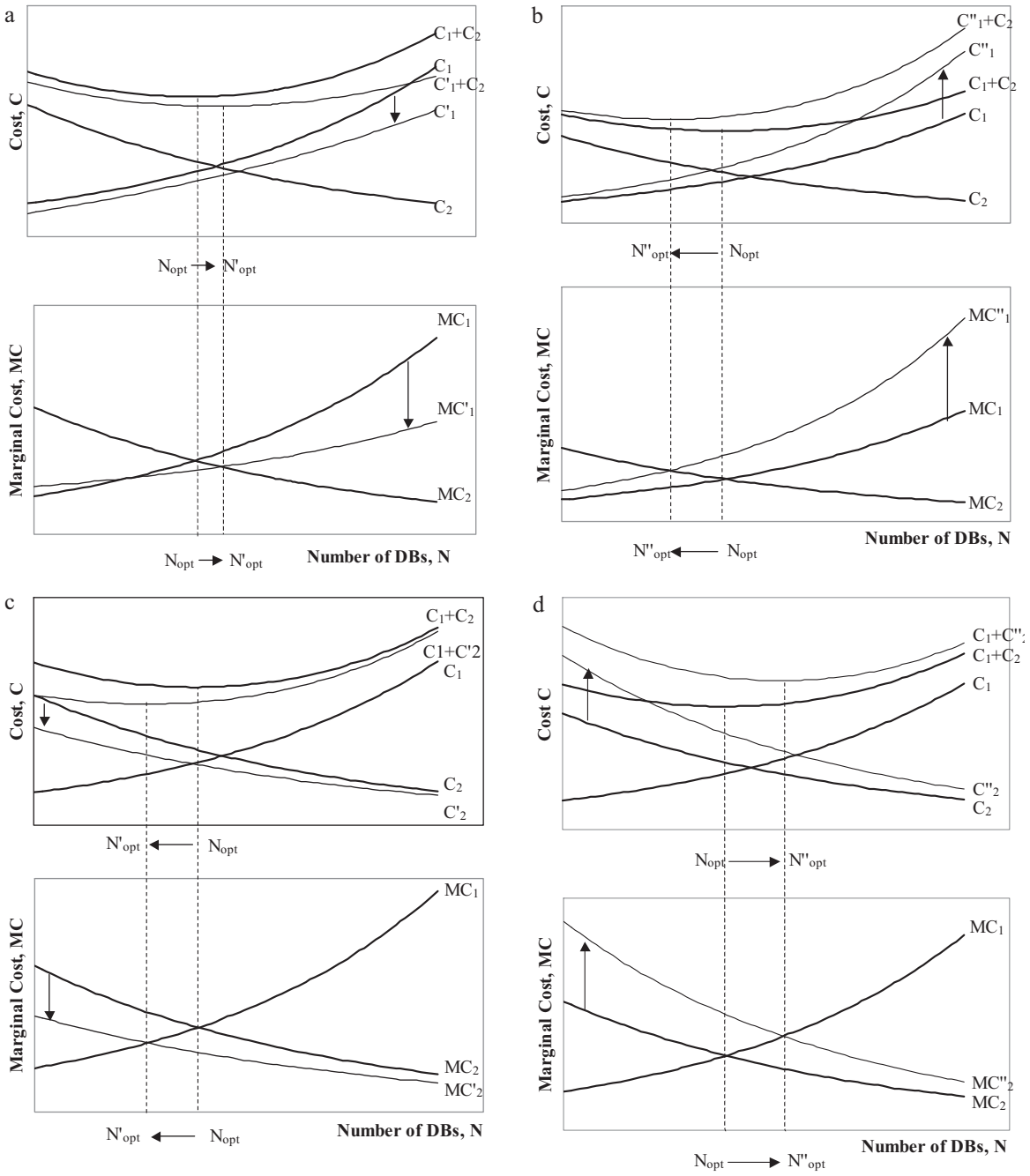

Fig. 9. Shifting of optimal number N_{opt} of differentiated biosensors (DBs) when an innovative biosensor with the following characteristics is introduced into the detection system: (a) cheaper and (b) more expensive in development/production/application, (c) more and (d) less resistant to interference.

The optimal number N_{opt} of DBs, and consequently of segments, can be determined at minimum cost $C(N) = C_1(N) + C_2(N)$, where C_1 is the cost component due to segmentation of the pipeline (and setting/maintaining the corresponding number of DBs) to obtain higher information granularity and C_2 is the cost component due to risk for undetected pipeline failure, all expressed in economic terms to ensure additivity. C_1 is an increasing function of N with an increasing rate (i.e., $dC_1/dN > 0$, $d^2C_1/dN^2 > 0$), for the reasons quoted in the previous paragraph. C_2 is the decreasing function of N with an increasing algebraic or a decreasing absolute rate (i.e., $dC_2/dN < 0$, $d^2C_2/dN^2 > 0$ or $d|dC_2/dN|/dN < 0$), because of the Law of diminishing returns, equally valid in Economics and Engineering/Technology, stating that (beyond a point, defined as the upper limit of the sub-optimal region) input increments produce lesser output increments, under the *ceteris paribus* clause. C_{min} is determined as the equilibrium point of the trade-off between the conflict partial dependent variables C_1 and C_2, while N_{opt} is the corresponding abscissa, where $dC/dN = 0$ or $d(C_1 + C_2)/dN = 0$ or $dC_1/dN + dC_2/dN = 0$ or $MC_1 = MC_2$, MC standing for marginal cost, i.e., $MC_1 = dC_1/dN$ and $MC_2 = |dC_2/dN|$.

In case that an innovative (less expensive in development/production/application) biosensor enters the detection system, C_1-curve moves downwards becoming also more flat, since scale economies are more expressed for higher N-values; as a result, N_{opt} is shifting to N'_{opt}, where $N'_{opt} > N_{opt}$, as shown in case [a] of Fig. 9. The opposite effect will take place if a more expensive biosensor enters the detection system, with N_{opt} shifting to N''_{opt}, where $N''_{opt} > N_{opt}$ (case [b] in Fig. 9). In case that the innovative

biosensor is more resistant to interference, C_2-curve moves downwards becoming also more flat, since improvement in risk is more expressed for lower N-values; as a result, N_{opt} is shifting to N'_{opt}, where $N''_{opt} < N_{opt}$, as shown in case [c] of Fig. 9. The opposite effect will take place, if a biosensor less resistant to interference enters the detection system, with N_{opt} shifting to N''_{opt}, where $N''_{opt} < N_{opt}$ (case [d] in Fig. 9).

Evidently, the combinations [a and d] and [b and c] result with certainty to application of more and less biosensors, respectively; on the other hand, the combinations [a and c] and [b and d] may result to more or less biosensors, depending on the degree of N_{opt}-shifting that each change brings about separately. Even the most favorable combination [a and c] does not give an *a priori* indication of the direction that N_{opt} will follow, although the moving of C_{min} to a lower level is certain, forming actually a strong incentive for biosensor innovation. Similarly, the most unfavorable combination [b and d] does not give an *a priori* indication of the direction that N_{opt} will follow, although the moving of C_{min} to a higher level is guaranteed, forming actually a strong contra-incentive for niche expensive technologies that are not suitable for field applications [49]. It is worthwhile noting that, when the direction of C_{min} movement is certain the N_{opt} shifting is uncertain and *vice versa*: when the N_{opt} shifting is certain the direction of C_{min} is uncertain.

The designing of pipeline monitoring schemes utilizing the biosensing and segmentation approach presented herein can be applied also in the case of offshore networks, like the Greece-Italy pipeline (about 807 km total length, of which 590 km will be onshore in Greece and more than 217 km will be laid on the sea bed of the Ionian Sea). The monitoring of undersea networks presents increased complexity since microbiologically influenced corrosion (MIC) or biocorrosion, a major cause of ruptures or holes on the metal, is difficult to detect or assess. Most MIC studies have focused on bacterial involvement (sulfate reducing bacteria, sulfur oxidizing bacteria, manganese-oxidizing bacteria, etc.); however, other single-celled organisms, such as fungi, yeast, and diatoms, can influence corrosion. These organisms co-exist within a biofilm matrix on metal surfaces, functioning as a consortium, in a complex and coordinated manner. Despite decades of study on MIC, it is still not known with certainty how many species of microorganisms contribute to corrosion, while researchers continue to report on the formation of biofilms by an ever-widening range of microbial species. To understand the causes and effects of MIC requires an understanding of the interaction of both, the metallurgical and electrochemical aspects of corrosion, as well as the microbial aspects of MIC-related microorganisms. Effective and efficient monitoring strategies can result from the understanding of microbiological activities and their effect on corrosion reactions.

The authors are currently working on a project for the undersea pipeline monitoring of the Greece-Italy routing, employing a knowledge based approach to MIC by means of creating a network of biosensors with a view to (i) elucidating/clarifying the relation between electrochemical and microbial synergistic effects leading to corrosion and (ii) monitoring the corrosion risk in undersea hydrocarbon storing/transporting facilities. In this case, biosensors may serve as both, microbial corrosion pathway identifiers (by qualitatively and quantitatively detecting either chain-species involved or metabolic products/by-products) and MIC prevention agents (by qualitatively and quantitatively detecting corrosive precursors and micro-environmental conditions that could potentially favour MIC processes).

5. Concluding remarks

Pipeline leakage detection continues to be a difficult issue because existing detection methods of guarding pipelines need improvement for more effective prevention of leaks and deterring third party intrusion into pipelines and plant facilities. The use of rapid, sensitive and selective biosensors may provide, in synergy with conventional leakage detection and applicable codes and standards, a reliable system for long-term pipeline network monitoring, provided that the biosensors are properly designed/developed/standardized and rationally placed/networked/maintained by the aid of operational research techniques. The proposed approach, focused primarily on the computer-aided multicriteria selection of suitable biosensor platforms and the tailored development of site- and target-specific detectors, has been successfully demonstrated to provide non-intrusive pipeline monitoring of a Greek network near Athens by acting as an early warning system for the presence of potentially dangerous gases in the atmosphere (i.e., hydrogen sulfide, mercaptan, methane).

It is worthwhile noting that, further to preventing gas releases, with various environmental effects (from odor pollution to photochemical smog at local level), knowing the exact way to effectively protect a system may affect its design *ab initio*, as it has been shown by the authors in the case of designing a gas absorption system on the basis of the metrological parameters of the measuring device used for emissions monitoring [197]. Last, but not least, knowing the added environmental load (due to leakage) on an already polluted area, may lead to the optimization of the monitoring network, as the authors have also shown in the case of early warning and prevention of photochemical episodes [198].

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