Recipients
Regional Council of Päijät-Häme,
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TANIA – PROJECT
REVIEW ON CURRENT *IN SITU* REMEDIATION TECHNIQUES

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RAMBOLL PÖYRY insinööritoimisto GRADIENTTI vuodesta 2004

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Team **Salla Selonen, Ramboll**
Aura Nousiainen, Pöyry
Katariina Koikkalainen, Ramboll
Sanna Pyysing, Pöyry
Julia Ruotsi-Turbaev, Insinööritoimisto Gradientti
Kirsti Määttä, Insinööritoimisto Gradientti

Reference 1510039503

Ramboll
Niemenkatu 73
15140 LAHTI
P +358 20 755 611
F +358 20 755 6201
www.ramboll.fi

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1. INTRODUCTION

1.1 TANIA-feasibility study

Interreg Europe-funded TANIA project (TreAting contamination through NanoremedIAtion) maps nanoremediation-based methods for the remediation of contaminated soil and groundwater as well as other new *in situ* techniques that have not yet been pushed through. The project was initiated on the 1st of January 2017 and will run until 31.12.2021. It involves partners from five different countries and has a total budget of 1 280 733 €. More information on the project can be obtained from the project site: https://www.interregeurope.eu/tania/.

In connection to TANIA project, Ramboll, Pöyry and Insinööritoimisto Gradientti were contracted by the TANIA-partners Regional Council of Päijät-Häme and the University of Helsinki to carry out a review of in situ remediation methods that have been used in the last five years. The review focuses on actual contaminated sites where *in situ* methods were used for soil or groundwater remediation. Although the TANIA project is primarily focused on nanoremediation-based methods, this review also considers other *in situ* techniques.

1.2 Categories of *in situ* remediation techniques

The currently used remediation methods can be crudely divided into three categories based on their mode of action.

1) Biological methods are based on biological processes. Biostimulation (stimulating the microbial degradation activity), bioaugmentation (addition of contaminant degrading bacteria), and anaerobic dehalgoenation rely on microbial degradation of contaminants. When soil is decontaminated by phytoremediation, two mechanisms are taking place. On one hand, contaminants may be bound to plant material, but degradation can also be enhanced due to the increased biological activity of the rhizospheric bacteria associated with the root system.
2) Chemical methods include above all chemical oxidation and reduction, where strong chemical oxidizers or reducers are injected into the contaminated environment. Other chemical methods rely on reducing the bioavailability of the contaminant by e.g. solidification or stabilization, where a contaminant is not removed, but rather locked in the soil by physically encapsulating it with a carrier matter, such as zeolite, fly ash or kaolinite.
3) Physical methods, such as aeration, thermal treatment, soil vapour extraction, soil washing, and pumping and treating all remove the contaminant by injecting, extracting or introducing a physical phase or force in the soil. Many of these treatments actually aid the biological remediation. Some other physical methods, like reactive barriers and isolation overlap with chemical methods. Electrokinetic method differs from the other physical methods. It is based on inducing an electric field in the soil. In many cases, the decontamination is a secondary effect, as chemical and biological degradation activities are stimulated.

1.3 Objectives

The objective of this study was to assess the current use of available *in situ* techniques, their benefits, challenges and potential risks, and to identify the upcoming trends and novel methods in soil and groundwater remediation. Special emphasis was put on nanoremediation. This study attempts to map the field experience on all bioremediation methods globally, as well as to gain insight on the general knowledge and experience of consultants, scientists and contractors, and public authorities working in the field of soil and groundwater remediation.

2. MATERIALS AND METHODS

The data for this study was collected in the form of a questionnaire. The languages of the questionnaire was English, Finnish and Russian. The subjects in the questionnaire were divided into four parts:

1) Background information of the responder
2) Information regarding the methods used in the field (method, contaminant, year, the success of the treatment, remediation costs and need for monitoring)
3) Evaluation of the methods (benefits, challenges, risks)
4) Future prospects

3. RESULTS OF THE QUESTIONNAIRE SURVEY

1.1 Survey respondent data

The data presented below is based on 28 individual responses to the survey. The responders represent 69,5% consultants, 11% researchers, 12,5% authorities, and 7% contractors. The sites the responders considered were situated mainly in Europe (79%) and North America (17%), and answers regarding single responses from South America and Australia and Oceania were obtained. No replies originated in Asia or Africa. Thus, the survey results can be considered Europe-based, and mainly from the point of view of a consultant (Table 1).

Table 1. Number of responses on the questionnaire from different fields of operation and countries.

	Field of operation			
	Consultant	Constructer	Authority	Research
Finland	5	1	3	1
United Kingdom	5			
Germany				1
Italy	2			
Spain				1
Belgium	1			
United States	5			
Brazil	1			
Australia	1			
Russia		1		
Total	**20**	**2**	**3**	**3**

Table 2. Number of reported remediation projects and the average of the proportion of in situ remediation projects from all remediation projects of the responders.

	Number of remediation projects			
	Soil	Groundwater	Soil and groundwater	In situ projects from all remediation projects (%)*
Finland	59	10	15	17 %
United Kingdom	10	20	4	30 %
Germany	4	4	4	
Italy	3	0	7	
Spain	0	1	0	
Belgium	2	6	2	
United States	7	10	17	55 %
Brazil	0	4	0	
Australia	3	1	1	
Russia	4	0	19	
Total	**92**	**56**	**69**	**56 %**

*The researchers (the percentage for all researchers 100 %) and the data including one or two answers per country were excluded from the results concerning individual countries

1.2 Used *in situ* methods

The most common method to treat contaminants *in situ* was groundwater pumping and treating (58%) and biostimulation (24%). The number of sites treated with pumping and treating has been rather stable, whereas a significant increase in biostimulation was observed in the year 2017. Reactive barriers, solidification and phytoremediation were amongst the less used techniques (less than 10 cases in five years) (Figure 1).

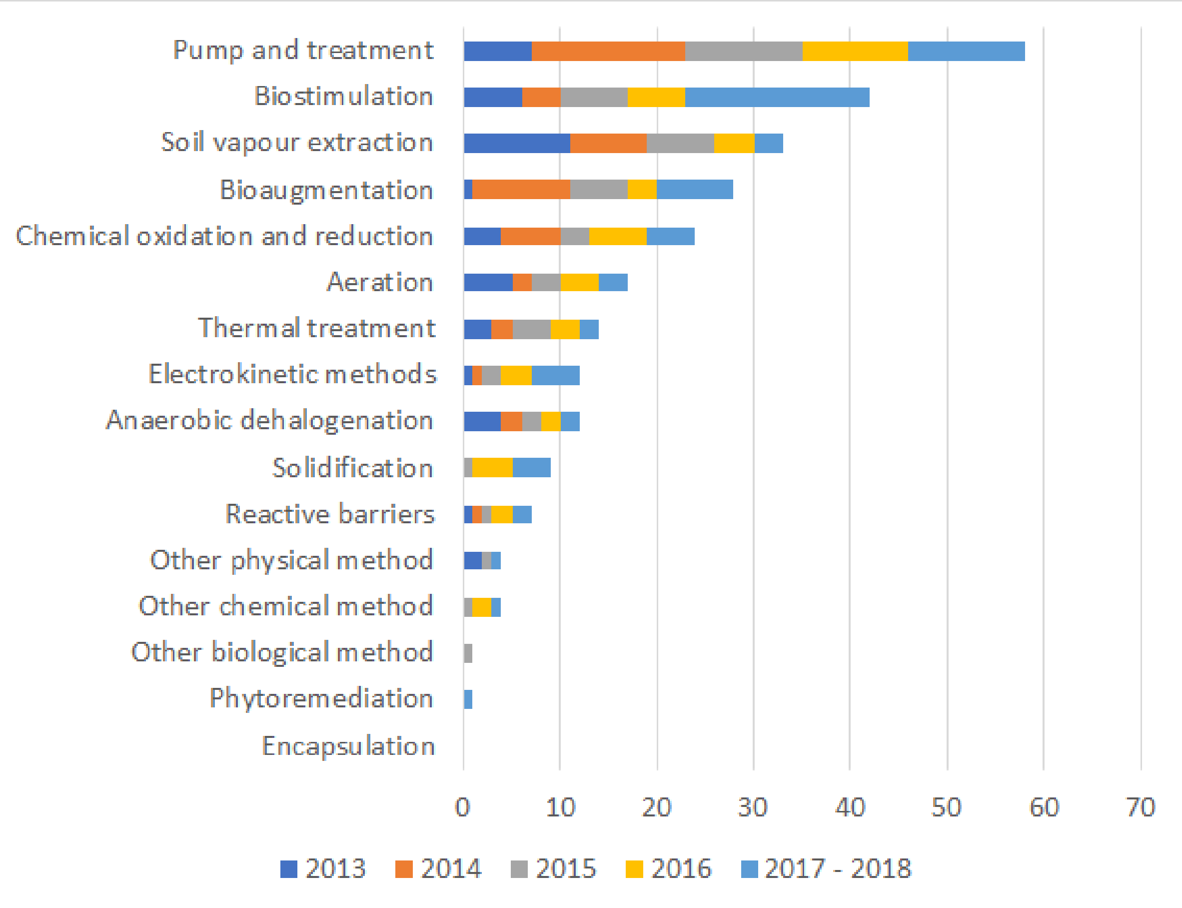

Figure 1. Number of sites remediated with different methods between 2013 and early 2018.

Pumping and treating was predominantly carried out in oil hydrocarbon remediation. Oil hydrocarbons were also the most common contaminants removed by biostimulation, as well as other petroleum industry related contaminants, such as BTEX and oxygenates. A few methods, such as electrokinetic methods, pump and treatment, and biostimulation were used to degrade PAH compounds. No *in situ* solution was used for PCDD/F, PCB or other POP compounds, nor pesticides or biocides (Figure 2).

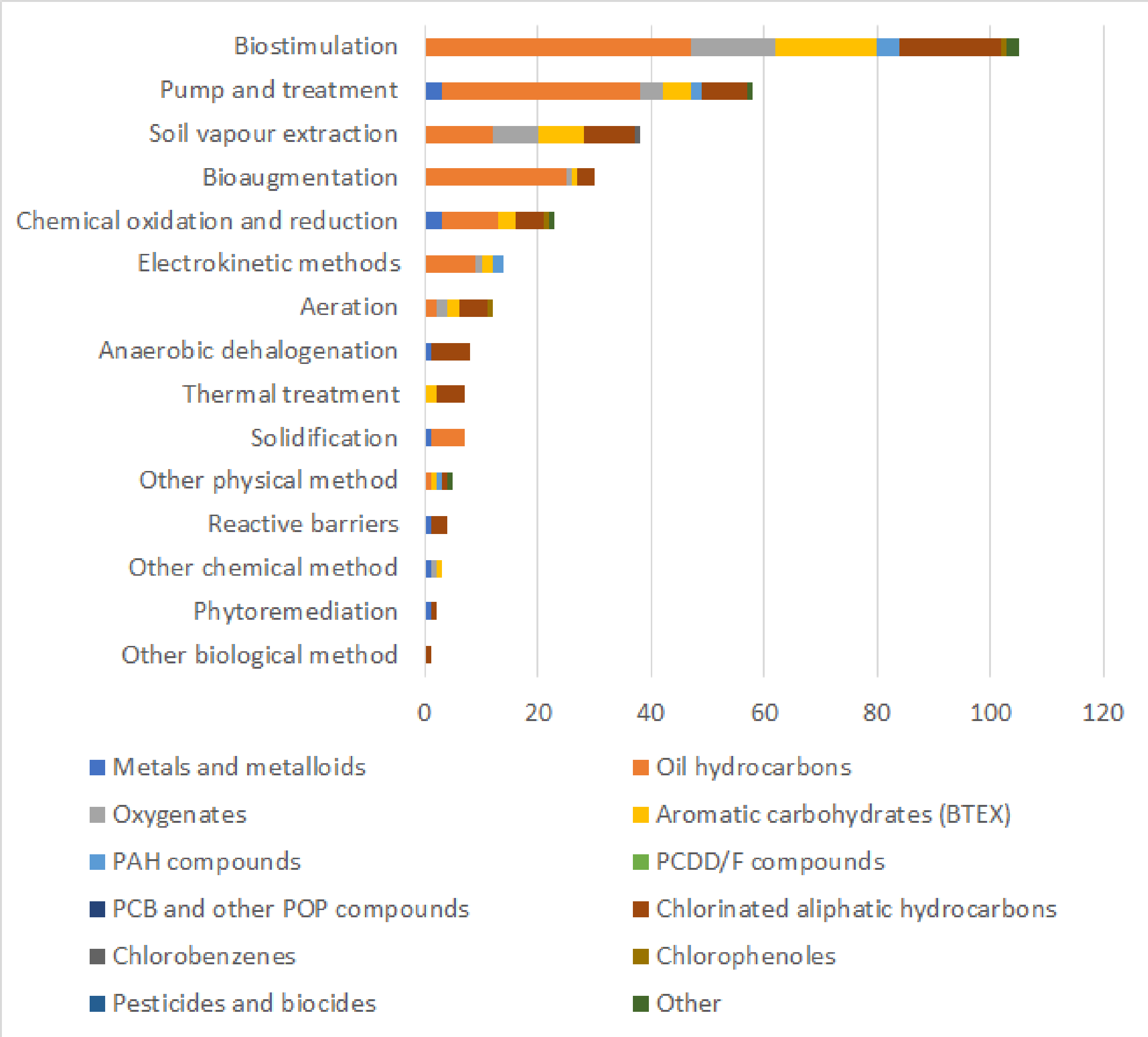

Figure 2. Contaminants remediated by *in situ* methods.

1.3 Success and value analysis

Method selection is always dependent on site properties. Most often the driver for decision making is the probability of meeting the remediation targets. The most commonly chosen *in situ* methods, biostimulation and pumping and treating, had the best remediation success rates (Figure 3).

From the most often used methods, biostimulation was deemed the most inexpensive: 82% of the sites were remediated with less than 100 €/t. The treatment times vary, 60% of the sites were remediated in less than two years, with a lengthy monitoring period up to 5 years (83% of the cases) (Figures 5 and 6). However, the remediation targets were entirely met in only 30% of the cases, and 18% of the sites had less than 50% contaminants removed.

Pumping and treating was more effective than biostimulation, with 55% of sites meeting the remediation targets. However, the duration of the remediation, as well as remediation costs and the time needed for monitoring varies substantially.

Chemical oxidation and reduction had one of the highest success rates (64% of sites met the remediation targets). Chemical oxidation and reduction costs varied greatly, and depending on the site properties and technical issues it can be either inexpensive (60% of cases costs were below 100 €/t) or expensive. Besides a few rare methods, chemical oxidation and remediation is the least time consuming *in situ* method, 67% of the sites were remediated in less than a year (Figure 5). The monitoring period was approximately the same as with biostimulation (Figure 6).

Good results were also obtained by commonly used soil vapour extraction and pumping and treating, which were second and third most effective methods both in meeting the targets and in remediation costs. Both methods require long treatment and monitoring times can be extensive, up to 5 years in 67% of the cases (Figures 5 and 6).

A few methods acquired only a few answers in the query, but 100% of the remediation targets were met. These methods are thermal treatment, solidification, phytoremediation and bioaugmentation. Due to the limited data, it is difficult to compare these methods reliably. However, the data collected here suggests that

- Thermal treatment is a common choice for remediating chlorinated aliphatic hydrocarbons, it is expensive but effective and reasonably fast.
- Solidification is inexpensive method, where treatment is fast and monitoring time short or nonexistent
- Phytoremediation is cheap but time consuming. It should also be noted, that the land cannot be used for other purposes during the treatment period
- Bioaugmentation is most commonly used for oil hydrocarbon contamination. It is expensive and time consuming.

Electrokinetic methods were used in 14 cases, predominantly in oil hydrocarbon remediation. The method has moderate success rates, is relatively inexpensive and fast.

A lot of variation between results was seen in reactive barrier use, anaerobic dehalogenation and aeration. Anaerobic dehalogenation is a method of choice for chlorinated aliphatic hydrocarbons.

No method queried here could be deemed entirely unsuccessful, but the least success was obtained using anaerobic dehalogenation (50% of the sites met less than 50% remediation targets). This method is almost predominantly used for chlorinated hydrocarbon degradation, which is more time consuming and technically challenging, as anaerobic reactions are slow, and the microbes capable of degrading chlorinated solvents are scarce.

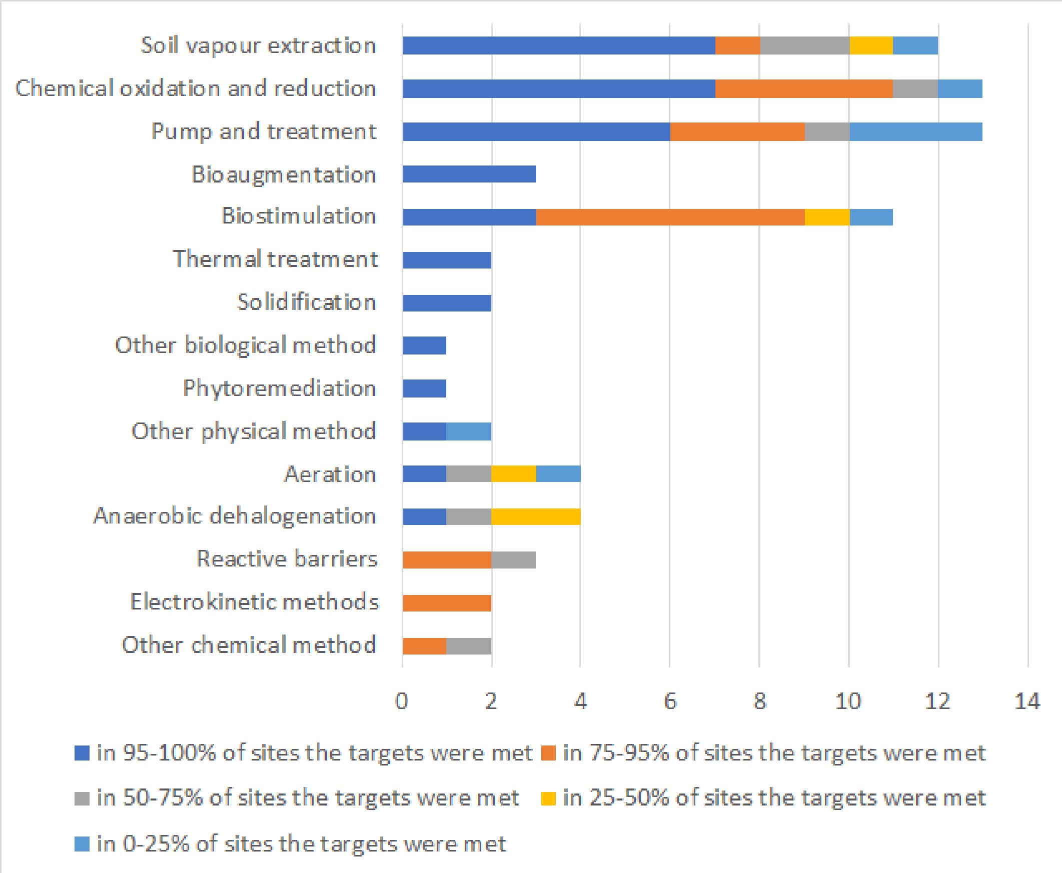

Figure 3. Success rates of the *in situ* remediation using different methods

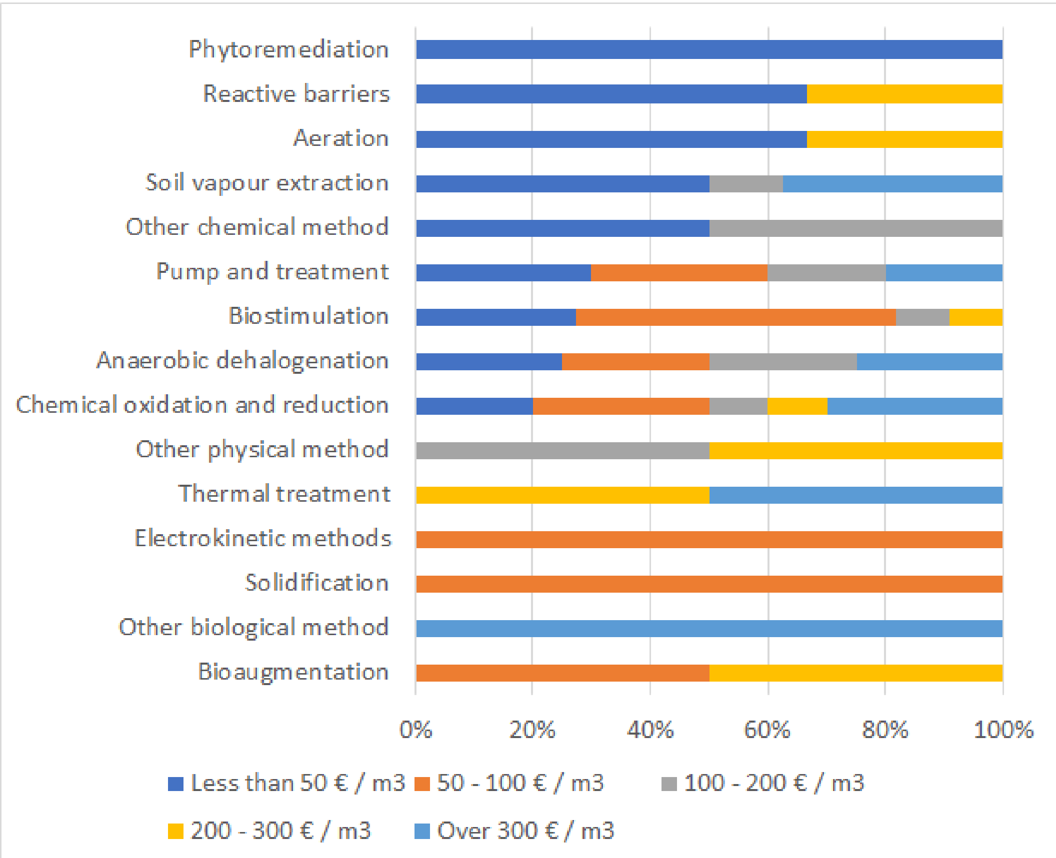

Figure 4. Remediation costs in different *in situ* remediation methods.

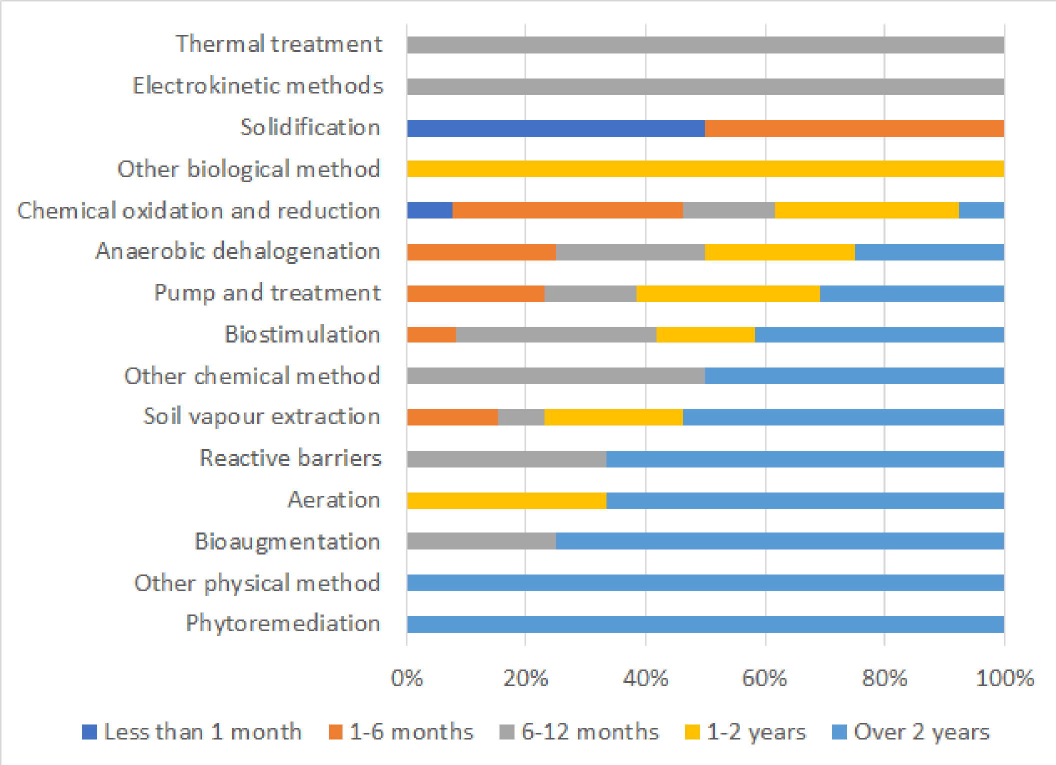

Figure 5. Duration of remediation

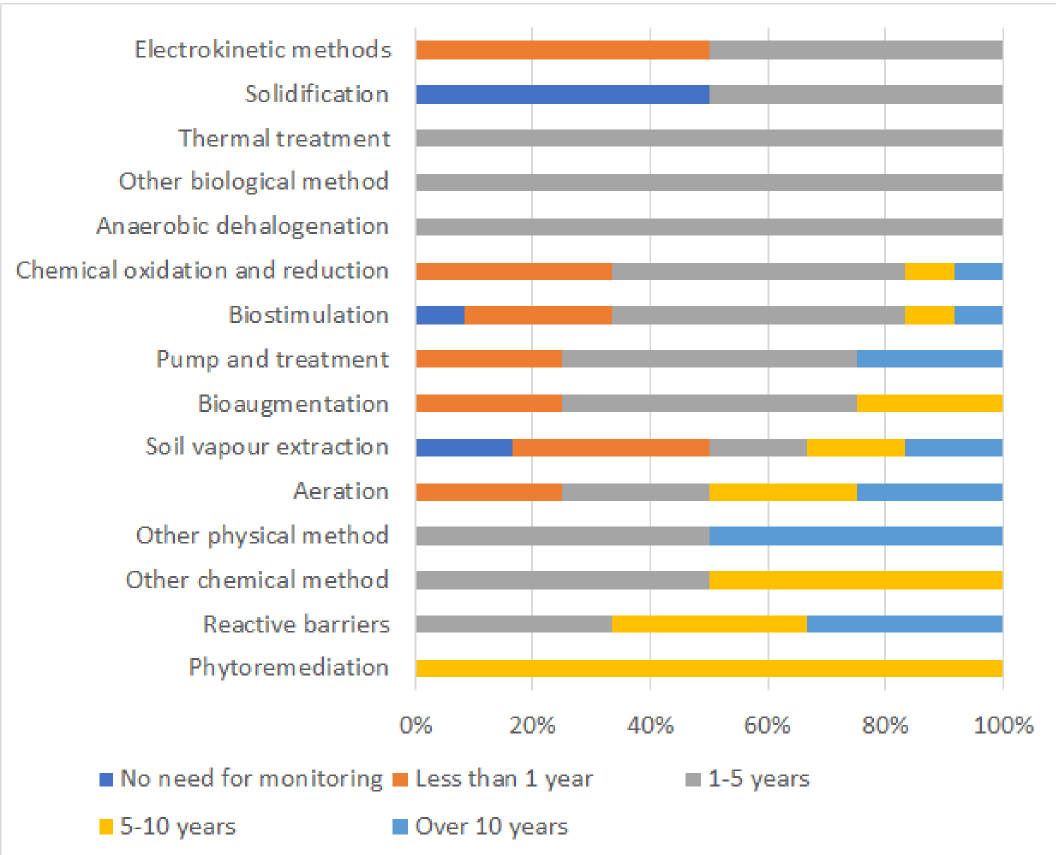

Figure 6. Need for monitoring

1.4 Evaluation of the methods

Commonly used, inexpensive and robust methods, such as biostimulation, pumping and treating, and chemical oxidation benefit from the fact that they are often used for decontaminating pollutants derived from oil industry, which are amongst the most easily degradable contaminants in the soil environment. Despite this, they have a long track record as mostly effective and cheaper options to excavation. Because these methods have been available for up to three decades, they are readily available, and along with soil vapour extraction, were also deemed the safest, and technically easiest (Figure 7). Controversially, these methods were also seen both as the most effective and most unreliable in reaching the remediation targets (Figures 7 and 8). This may reflect a more general tendency towards using *in situ* methods, where respondents may have a favorite technique.

All methods suffer for the usual *in situ* challenges, like the unpredictability of the results and long treatment and monitoring times. These issues were especially true to the methods where the contaminant is likely to migrate, such as in pumping and treating, and chemical oxidation, where the contaminant is often present in groundwater (Figure 8). Increased heavy metal mobilization while using chemical oxidation was mentioned as a complication several times in the query. Biostimulation and anaerobic dehalogenation were also challenged by long monitoring periods (Figure 8). Both methods require the activity of the microbial population, whose ecological structure and function are therefore difficult to predict. The least time-consuming method was chemical oxidation and reduction, followed by soil vapour extraction (Figure 7). Adverse change in the groundwater quality was seen as a risk when chemical oxidation and reduction and biostimulation were used.

Some methods, such as encapsulation, electrokinetic methods, and solidification suffer from poor availability. These methods have potential in the remediation of less degradable compounds such as chlorinated aliphatic hydrocarbons, PAH and BTEX compounds and metals and metalloids. They are in general fast, the remediation targets can be met reasonably well (more than 75%), and are inexpensive, but they suffer from technical difficulties and the uncertainty of the end result. However, the data acquired here is based on data with 12 remediated sites with electrokinetic methods, 6 by reactive barriers and none by encapsulation.

The data acquired by the survey study does seem to indicate that a few methods are better than the others. However, the data should be interpreted while keeping in mind that the methods are not directly comparable. Site properties have a profound impact on the successfulness of the treatment. Regardless of the method, if conditions like soil homogeneity, temperature, moisture content and particle size are adverse to that particular method, the remediation effectiveness can be significantly reduced and treatment times increased. Different methods have different requirements for the soil, e.g. thermal treatment and electrokinetic methods work best in silty, wet soil, whereas biostimulation, bioaugmentation, soil vapour extraction and chemical oxidation and reduction rely on porous soil, where the additives are transported in the microchannels in soil. Pumping and treating is only valid for groundwater remediation, and its success is therefore more difficult to predict. Anaerobic dehalogenation seems expensive and ineffective, but is in fact the most sensible choice for decontaminating chlorinated solvents. Phytoremediation does not seem lucrative in all sites due to the long treatment times, but if there is no pressure to use the plot of land in the near future, it is a sensible option. Sometimes, when the contaminated soil mass is very large, and especially if the contaminant is under a building, *in situ* remediation is the only possible remediation choice.

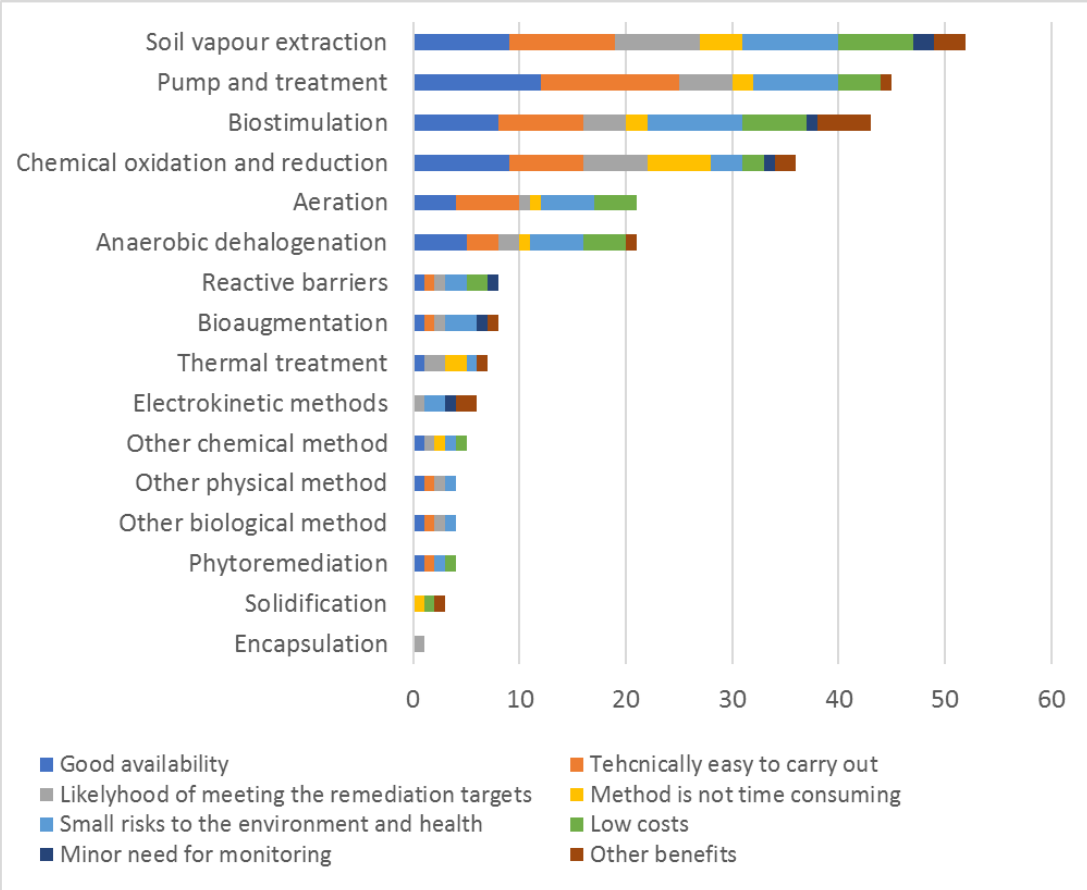

Figure 7. Benefits of the methods

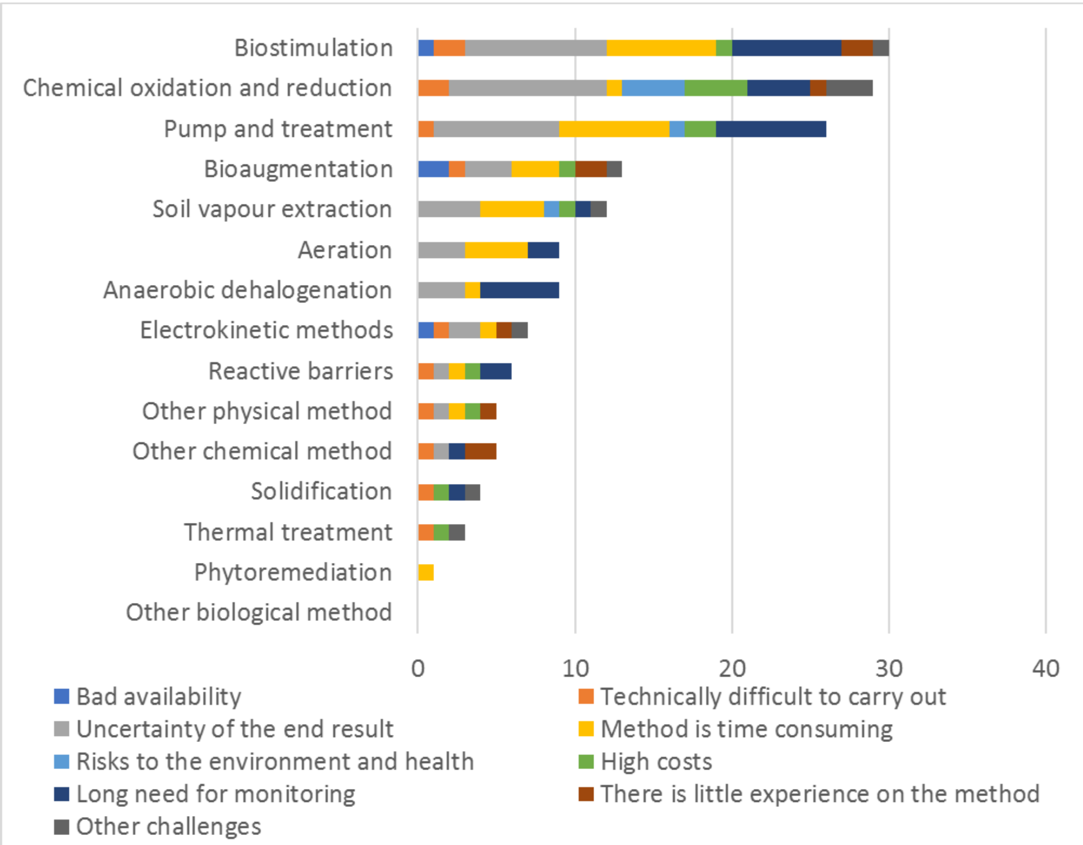

Figure 8. Challenges of the methods

1.5 Future prospects

All *in situ* methods have inherent unpredictability, and differences between treatment methods in this respect were small. Physical methods, such as thermal treatment, encapsulation, stabilization and solidification were seen as less uncertain. Of these, thermal treatment was deemed more expensive than any other *in situ* method. Stabilization and solidification, along with chemical oxidation and reduction were seen to contain the greatest risk to the environment. Otherwise *in situ* methods were perceived as safe (Figure 9).

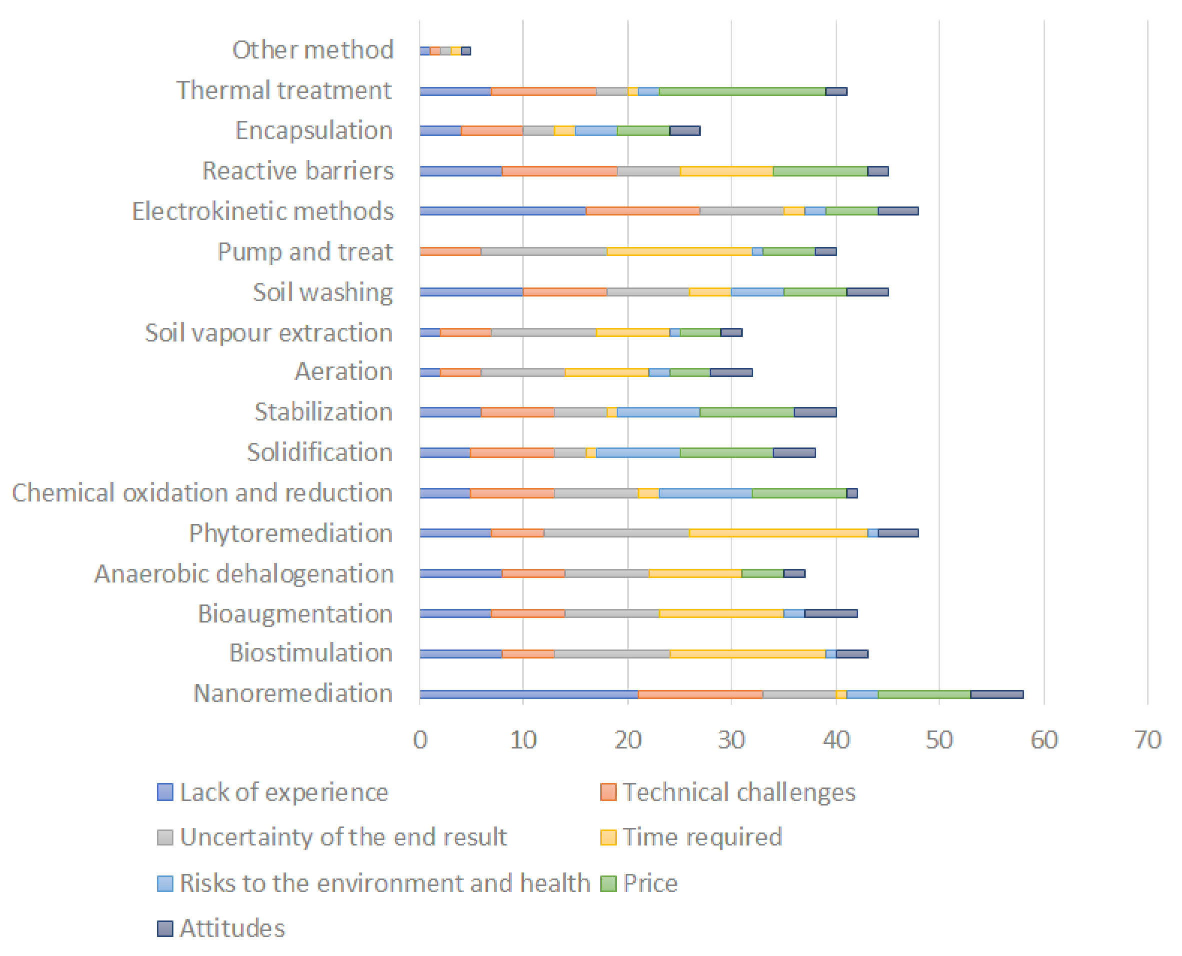

Figure 9. Issues limiting soil *in situ* treatments

Nanoremediation and the electrokinetic methods stood out as lacking in user experience. Only a handful of sites in the query were remediated by electrokinesis, and none at all with nanoremediation. Perhaps this will change in the near future, as nanoremediation has both been developed to a great deal in the past few years (Figure 10) and many responders see a great potential in its use in the following years (Figure 11).

Also some of the oldest *in situ* methods are being further developed, and seem to have a lot of future prospects. Biostimulation and anaerobic dehalogenation stand out in this examination, probably due to the new and upcoming technical advancements in distributing the additives to soil with probes and drills. Bioaugmentation, chemical oxidation, and perhaps oxidant/reductant use in reactive barriers, also benefit from this development.

Physical methods, such as solidification, stabilization, electrokinetic methods and encapsulation are considered somewhat promising, although they are not perhaps in the spearhead of further development.

Pumping and treating method seems to have reached its technical limit, and very little prospects as its further potential is seen. Also methods like soil vapour extraction, soil washing and aeration are not developing further. Some advances have happened in thermal treatment, but this is not reflected on the future prospects (Figures 10 and 11).

Additionally, some specific problems with *in situ* methods were pointed out in the questionnaire esponses. Some chemicals, like PCB:s and 1,4-dioxane, are new to bioremediation, and suffer from limited methodological options. Choosing the correct method for the sites requires high expertise, which limit the use of *in situ* methods. The lack of *in situ* constructors may also limit the choices available.

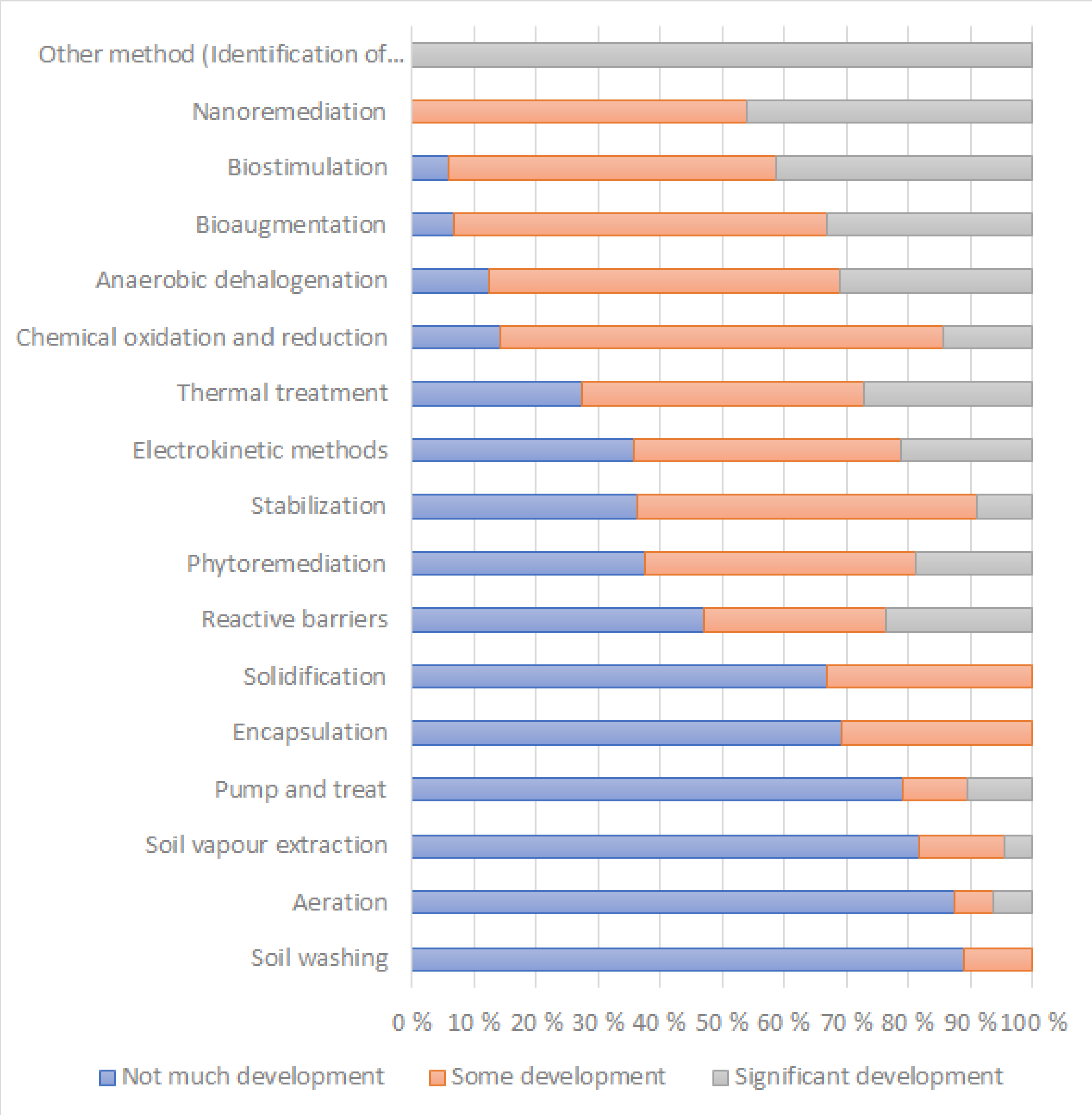

Figure 10. Recent development of the methods

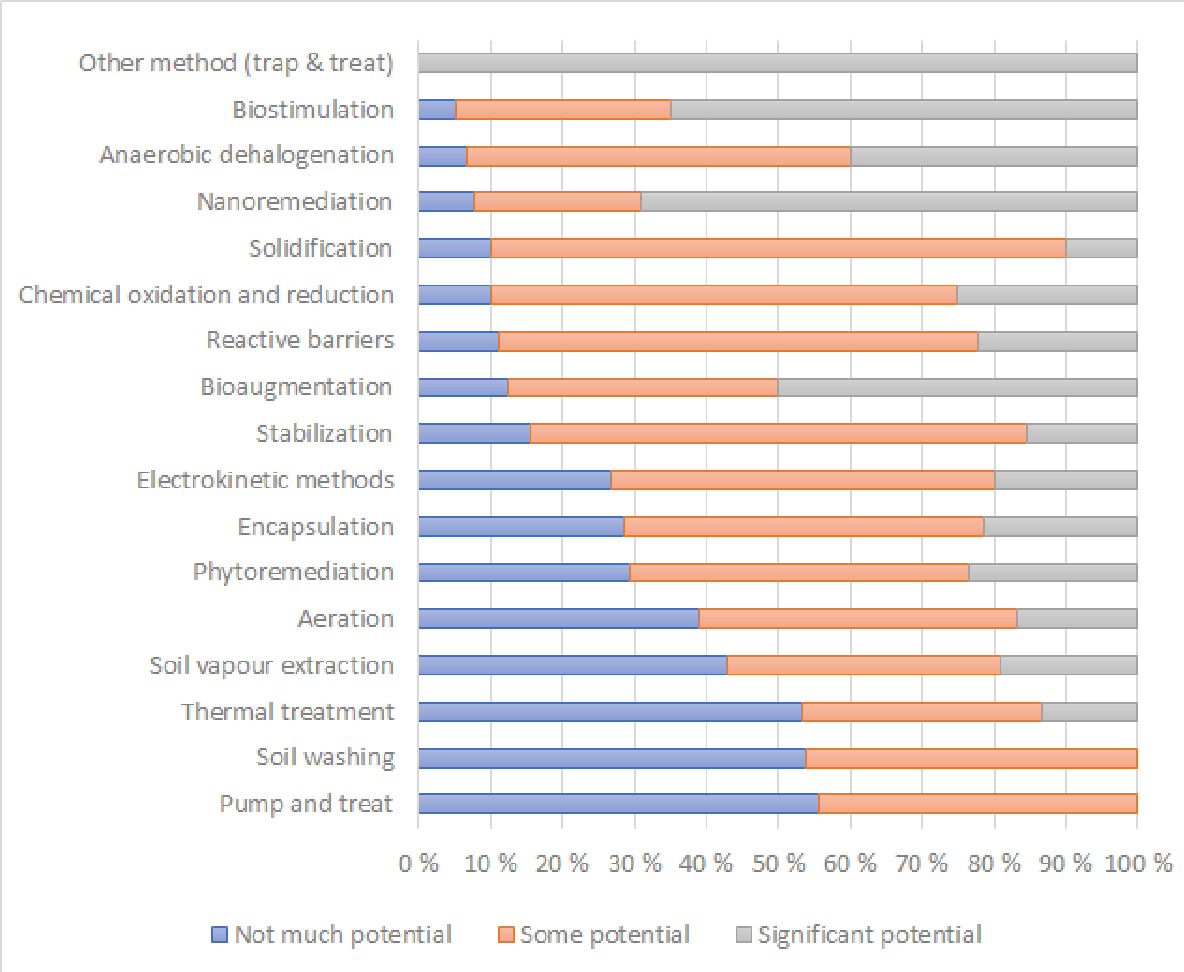

Figure 11. Estimated potential of the methods in the near future

4. OVERVIEW ON SOME NOVEL AND NEW DEVELOPMENTS IN SITU REMEDIATION TECHNIQUES

4.1 Nanoremediation

Nanoremediation means the utilization of nanoscale materials in soil or groundwater remediation. This entails nanoscale metals, especially zero valent iron (nZVI), which is the most commonly used nanomaterial used in remediation projects in Europe and the United states (Lefevre et al. 2016). In essence, it is an agent for chemical oxidation and reduction, but because of its small scale, it has a higher reactivity, permeability and mobility than most materials used today (Karn et al. 2009).

Nanoremediation is predominantly used by injecting slurry of nZVI in permeable reactive barriers (PRB). The particles can be bare ions and nFe-oxides, biometallics, polymerized to a carrier compound or emulsified. Approximately 70 Field-scale applications had been carried out until 2015 (Elliott 2016). The fast corrosion rates of nZVI produce a transient influx of electron acceptors or donors depending on the oxygen concentration on site. These reactions are utilized e.g. in halocarbon, pesticide, PCB, chlorinated phenols and other contaminants that degrade very slowly by microbiological methods.

There are many *in vitro* toxicity studies regarding to the effect of nZVI to soil biota. The toxic effects are due to the increase of the reactive oxygen species formed in Fe^{2+} and Fe^{3+} oxidation, and precipitation of iron oxides on the cell wall or inside the cell. Ferric ion exess in the pore water is transient, as Fe^{2+} and Fe^{3+} oxidase to insoluble ferrous minerals. Bacteria seem to be more susceptible to the toxic effects than fungi, as reviewed in Lefevre et al. (2016), and bacterial community shifts after nZVI treatments have been observed by Kirschling et al. (2010), Tilston et al. (2013), Kumar et al. (2014) and other studies.

Nanoremediation using nZVI is most promising of the novel remediation techniques. It can be used on several contaminants that are considered to be difficult by biological methods, and due to the small scale, it is more easily disseminated in the target environment. Despite its obvious benefits compared to other *in situ* techniques, the potential risks are poorly understood, and a proper evaluation, taking into account the impact to human health and the environment needs to be addressed before use in groundwater areas. Several full scale remediation projects have been carried out in the USA using bimetallic and emulsified nZVI, but the precautionary attitude has hindered their application in Europe (Mueller et al. 2011).

4.2 Novel electrokinetic methods

Electrokinetic methods are based on the utilizing the phenomena that an electric field generates in soil in contaminant remediation. This includes contaminant electro-osmosis, electromigration and to a lesser degree the electrophoresis of large particles. The field is created by installing positive and negative electrodes and an external power source. The electrochemical transportation and electrokinetics are a set of parallel chemical and physical reactions in the aqueous layer and on the diffusion layer of soil particles (Reddy et al. 2009). Because soil particles are most often negatively charged, they are surrounded by a layer of highly bound positively charged cations, which in turn are coated by diffuse layer of some anions, but mostly cations. In a low electrical field, the electroosmotic flow can enhance contaminant desorption. Additionally, the soil particles begin to act as redox-reaction provoking microelectrodes. The oxygen produced in these processes can benefit the microbiological degradation activity, and the free radicals enhance chemical degradation of the newly desorbed contaminants (Ramirez et al. 2014). Electrolysis generates an acidic zone around the anode, and basic to the cathode, which can be harmful to the microbial community. This obstacle has recently been overcome by changing the polarity of the electric field to adjust the pH, temperature and humidity according to the treatment (Ramirez (2014)

The most modern electrokinetic methods rely on the reactions on the soil particles rather than contaminant migration to the anode or cathode. Coupling electrokinetic methods with biological and chemical remediation techniques show some future potential. Promising results have been achieved with electrokinesis and bioaugmentation of diesel oil (Ramirez et al. 2015), hydrocarbons and heavy metals (Chilingar et al. 1997), diesel, fuel and waste oils (Martinez-Prado et al 2014). However, even paired with electrokinesis, bioaugmentation still suffers from its usual drawbacks, such as the adaptability of the introduced bacteria, predation, and microbial competition in the target environment. Competition can be mitigated by introducing the inoculant as consortia.

Electrokinetic methods have an advantage compared to biostimulation, chemical oxidation and reduction and bioaugmentation in that it is most effective in soils with low hydraulic conductivity (Reviewartsu).

4.3 Direct push injection

The factor limiting several methods, e.g. bioaugmentation, biostimulation, chemical oxidation, as well as nanoremediation, is that the contaminant and the remediating agent do not physically meet. In recent years, this shortcoming has been attempted to overcome by developing light drill rigs with a feeding system, where liquid remediation agent is injected in the soil using high pressure (In Situ Remediation Reagents Injection Working Group, 2009). Depending on the method and soil type, the injection pressure creates fissures due to pneumatic fracturing of soil, which allows the remediation agent to spread evenly in the contaminated mass. The injections do not require permanent well installations, and the treatment is usually carried out by a single injection. The technology has a background in geological and groundwater surveys, where it has been used for investigating hydraulic conductivity.

Direct push injection cannot be considered a novel technology itself, but its application in *in situ* remediation has overcome some issues in older *in situ* techniques, such as biostimulation, chemical oxidation and reduction, and bioaugmentation, making them more feasible than before.

5. PROSPECTS

The results of the questionnaire highlighted, that most of the *in situ* treatment methods used in the past five years are the same that have been used for a long time. As such, the novel methods were in the minority, with only a few mentions. All of these were new applications to old techniques. In the questionnaire, combining physical and biological methods, for example by trapping and treating, were used a few times, and have shown great promise. In this method, the bacterial consortium used in bioaugmentation is encapsulated in a physical carrier material that shields it from the competition of the indigenous microbial flora. Groundwater circulation with in-well sparging is another method where aeration is used in a novel way. Very complex combination of methods were used in sites with complex contaminant mixtures, or where bottlenecks for microbial degradation were removed after thorough investigation of the site properties.

It is likely that the next generation *in situ* remediation is a combination of several well-known methods, tailored to meet the needs of the site. Also, as more experience is gathered on *in situ* remediation methods, the end result is easier to predict.

In the questionnaire, a great deal of potential was seen in using nanomaterials in remediation. The global challenge with this method has been the possible associated toxicological and ecotoxicological risks as well as local legislation. The use of nanomaterials especially in groundwater areas needs more research in order to fully comprehend the risks involved. Despite this, nanomaterials are used in the United States, and as more experience is gained, the European region is likely to follow suit.

6. CONCLUSIONS

The shift from the use of single techniques to site-specific tailored solutions for each site has been a major trend in *in situ* remediation in the past five years. New and upcoming solutions like direct push injection and electrokinesis with frequently changing field polarity entail technical advancements to old methods. Nanoremediation by nanoscale ZVI is another megatrend which, as soon as insufficient knowledge about its potential toxicity is reached, has created a lot of expectations. In general, *in situ* remediation techniques are seen as increasingly useful. They are often cheaper, the end results are increasingly easier to predict, they are environmentally sound – and in some cases, the only viable option to decontaminate soil and groundwater.

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